23.0
EVALUATION OF NITROSOMORPHOLINE

23.1 PHYSICAL AND CHEMICAL PROPERTIES

Data on the physical and chemical properties of nitrosomorpholine were unavailable. To the best of our knowledge, no nitrosomorpholine is deliberately manufactured or used in the U.S. This review has therefore focused on morpholine, the immediate precursor of nitrosomorpholine.

23.2 DIRECT PRODUCTION IN CALIFORNIA

As of 1977, only one company manufactured morpholine in the United States (SAI, 1980). We were unable to contact this producer at either of its facilities, which are in Texas. This company either does not manufacture the chemical at the former sites or is producing under a different name. It remains to be determined whether production of morpholine has ceased in the United States. In either case, there appears to be no California production of the compound.

23.3 INDIRECT PRODUCTION AND EMISSIONS IN CALIFORNIA

As discussed in Section 23.8, all ambient nitrosomorpholine is probably formed in the atmosphere by the reaction of nitrous acid with morpholine or by OH-initiated photooxidation of morpholine. Data are presently not available on reaction rates for conversion of morpholine to nitrosomorpholine.

23.4 INDUSTRIAL USE AND EMISSIONS

The most recent data available on the consumption of morpholine in the U.S. are from 1978 (SAI, 1980). In 1978 morpholine was used as an intermediate for rubber accelerators (35 percent), corrosion inhibitors (30 percent), optical brighteners (10 percent), and self polishing waxes and polishes (10 percent). Seven percent of production was exported. Another eight percent was used in miscellaneous minor applications, which include the pharmaceutical industry, deodorants, shampoos, cosmetics, and disinfectants.

In 1978, rubber accelerators were not produced in California. However, 33 facilities on the Pacific Coast produced optical brighteners, although we do not know at present how many of them are located in California. At best, emissions from optical brightener production can be considered minor; only 460 lb/yr morpholine were used at all 33 sites.

To obtain an upper bound estimate of morpholine emissions, let us assume that the total amount of morpholine used in corrosion inhibitors (7.5 MM lb) and polish and wax formulations (2.5 MM lb) is released to the atmosphere. We further assume that the loss from these products is distributed among the states in proportion to state populations. Some of these products containing morpholine are consumer items and some have industrial uses. We do not know the proportion in each use, nor how precise the estimate of proportionate distribution by state is likely to be. Nonetheless, this is a reasonable first-cut estimation of the release of morpholine from these products. Thus, the amount of morpholine released to the air in California is estimated to be:

$$\begin{aligned}\text{California emissions} &= (10\ \text{MM lb})(0.11)\\ &= 1.1\ \text{MM lb}\end{aligned}$$

Surveys of tire manufacturing plants have found levels of nitrosomorpholine ranging from 0.5 to 27 μg/m3, which approximates a daily human exposure between 50 and 250 μg. These concentrations probably resulted from contamination of the accelerator with trace levels of bismorpholinecarbamylsulfenamide. Measurable levels of nitrosomorpholine have also been found inside leather tanneries (Ember, 1980).

23.5 CONSUMER USE AND EMISSIONS

Some releases of morpholine probably occur from a variety of consumer products which contain this compound, such as pharmaceuticals, deodorants, shampoos, cosmetics, and disinfectants. A search of current literature and formularies identified the following morpholine-containing products (morpholine contents in parentheses): porcelain, marble and tile cleaner (up to 2 percent); furniture and wood polish (up to 30 percent); leather and vinyl cleaner (1 percent); aerosol oven cleaner (0.2 percent); and aerosol chrome polish (2 percent) (Ash and Ash, 1982). Releases from these products are likely to be smaller than those due to use of morpholine in production of rubber accelerators and corrosion inhibitors. Releases are dispersed and likely to be gradual.

The potential for emissions of nitrosomorpholine from materials used in new automobiles was tested recently by Dropkin (1985), who sampled three cars as their interior temperatures rose from "ambient" to 60°C. Samples were collected on Thermosorb adsorbent. According to Dropkin, low concentrations of N-nitrosomorpholine were measured in the car interiors during the heating process, but higher levels were measured outside of the cars. In a study reviewed by Ember (1980), up to 2.5 $\mu g/m^3$ of nitrosomorpholine was detected in automobile interiors. The mean value for 38 new cars was 0.67 $\mu g/m^3$.

23.6 EMISSION SUMMARY

Emissions of morpholine are responsible for the production of nitrosomorpholine, although, to the best of our knowledge, no ambient concentration data are available. No direct production of morpholine exists in California. Optical brighteners may be produced in California, but emissions from this source are minor. The major sources of emissions of morpholine are likely to be from the use of corrosion inhibitors and waxes and polishes. We estimate that a maximum of 1.1 MM lb were released in California in 1978.

Specific point sources of morpholine that increase concentrations of nitrosomorpholine in the work setting are rubber tire manufacturers and leather tanneries. New car interiors are another localized source of nitrosomorpholine. A variety of consumer products may contain small amounts of morpholine, but are unlikely to be used in large enough quantities at one location to produce measurable concentrations of nitrosomorpholine.

23.7 SUMMARY OF AMBIENT CONCENTRATION DATA

No ambient concentration data are available for nitrosomorpholine.

23.8 ATMOSPHERIC CHEMISTRY

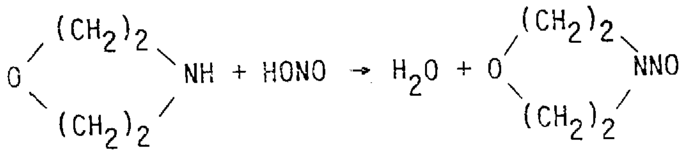
23.8.1 In Situ Formation

All nitrosamines may be formed in the atmosphere by reaction of nitrous acid with amines at night:

$$R_2NH + HONO \rightarrow R_2NNO + H_2O$$

and by OH-initiated photooxidation of amines during daytime. There has been no experimental study of nitrosomorpholine formation by either pathway. The mechanisms outlined below are based on those discussed in detail in Chapter 13 for dialkylnitrosamines. All pertinent references are also listed in Chapter 13.

Reaction of morpholine with nitrous acid yields nitrosomorpholine:



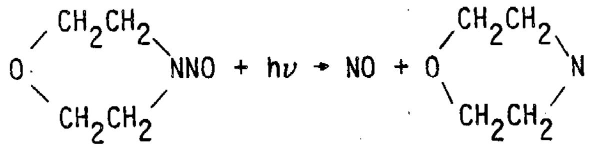
For morpholine, as for other secondary amines, this reaction is expected to take place in the atmosphere if the precursors are present at night. Levels of HONO of up to 8 ppb have been measured in Los Angeles air. Levels of morpholine have not been measured, in California or elsewhere.

The second possible pathway for in-situ formation of nitrosomorpholine involves the reaction of morpholine with OH. The rate constant for this reaction has not been measured, but is estimated to be close to that for the reaction of OH with other dialkylamines, i.e. about 5×10^{-11} cm^3 $molecule^{-1}$ sec^{-1}. A tentative reaction scheme, based on that derived from experimental data for dialkylamines, is presented in Figure 23.8-1. H-atom abstraction from the N-H bond (pathway A) is expected to account for about 30 percent of the overall OH-morpholine reaction. The amino radical thus formed then reacts with NO to form nitrosomorpholine, and with NO_2 to form a nitramine and other products. As for other amino radicals, reaction with O_2 is expected to be slow, e.g. $k_{O_2}/k_{NO} \sim 1.5 \times 10^{-6}$ and $k_{O_2}/k_{NO} \sim 4 \times 10^{-7}$. As for other secondary amines, H-atom abstraction from C-H is expected to compete with H-atom abstraction from N-H. For morpholine, two alkyl radicals may form (pathways B and C), as compared to only one in dialkyl amines. Further reactions of these alkyl radicals lead to 2-oxomorpholine (pathway B), 3-oxomorpholine (pathway C), as well as ring opening radicals leading to formaldehyde and other products.

As for the morpholine-HONO reaction at night, data on ambient levels of morpholine are required to assess the importance of the OH-morpholine reaction as a daytime pathway for nitrosomorpholine production. Such data are not available at the present time.

23.8.2 In Situ Removal

Nitrosomorpholine is expected to photolyze rapidly in sunlight:



with the amino radical reacting with O_2 and NO_x as is shown in Figure 23.8-1. The photolysis rate constant is estimated to be about 0.12 min^{-1}, and corresponds to atmospheric half-lives of 30 to 60 minutes. As a result, nitrosomorpholine is not expected to accumulate in the atmosphere during daytime.

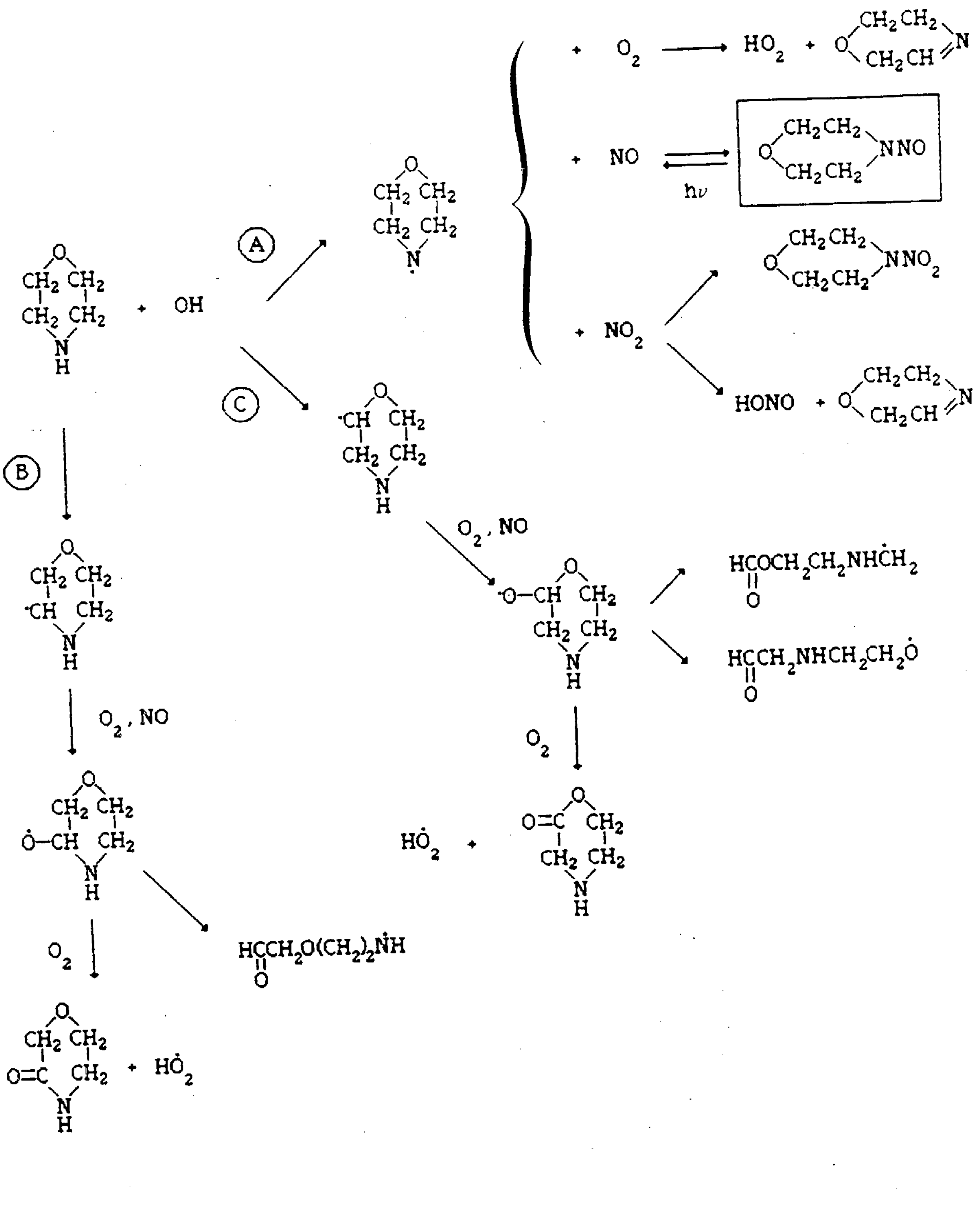


Figure 23.8-1. OH-Morpholine Reaction.

23.9 REFERENCES

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Dropkin, D. 1985. *Sampling of automobile interiors for organic emissions.* U.S. Environmental Protection Agency, Atmospheric Sciences Research Laboratory, Research Triangle Park, NC, EPA-600/3-85-008 (NTIS: PB85-172567).

Ember, L. 1980. "Nitrosamines: assessing the relative risk," *Chemical and Engineering News* 58(13): 20-26.

SAI (Systems Applications, Inc.). 1980. *Human exposure to atmospheric concentration of selected chemicals: Volume 2.* Prepared for the U.S. Environmental Protection Agency, Research Triangle Park, NC (NTIS: PB81-193260).

24.0

EVALUATION OF PHENOL

24.1 PHYSICAL AND CHEMICAL PROPERTIES

Phenol and its nitro derivatives are crystalline solids at ambient temperatures. Tables 24.1-1 through 24.1-5 summarize some of the physical and chemical properties of phenol, 2-nitrophenol, 4-nitrophenol, 3-nitro-2-hydroxytoluene, and 5-nitro-2-hydroxytoluene.

24.2 DIRECT PRODUCTION IN CALIFORNIA

In the U.S. over 96 percent of phenol is produced by the cumene peroxidation process (Lesh and Mead, 1985), and the remainder by the oxidation of toluene (SAI, 1980). Chevron U.S.A. in Richmond formerly produced phenol but ceased phenol production in 1982 (Williams, 1986). The ARCO Chemical Company in Carson used to manufacture phenol, but shut down its BTX unit in 1983 (Anon., 1986). The only remaining phenol manufacturing facility in California is a plant in Santa Fe Springs which was formerly owned by Ferro Corporation and is now operated by P.M.C. Specialties Group (Kaufman, 1986).

In a typical plant which produces phenol from cumene, phenol is emitted from the production process, from the storage tanks, and from fugitive releases (SAI, 1980). Production losses can occur during cumene peroxidation, cleavage, and product purification (Lesh and Mead, 1985).

Emissions from the Ferro/P.M.C. Specialties Group facility were estimated to be 11,988 lb in 1978 (Bloomhardt and Pelland, 1985; SAI, 1980). Phenol production data at the Santa Fe Springs plant for 1984 and 1985 are proprietary and cannot be reported. However, using the average phenol production for these two years, and emission factors adapted from the literature, we calculate emissions of 2,447 lb/yr (1.2 tons/yr) for 1984 and 1985.

Table 24.1-1

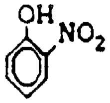
CHEMICAL DATA SUMMARY FOR PHENOL

Property	Value for Phenol
CAS Registry No.	108-95-2
Synonyms	Carbolic acid, phenylic acid, oxybenzene, phenyl hydroxide, hydroxybenzene
Molecular Weight	94.11
Molecular Formula	C_6H_6O
Molecular Structure	
Physical State at STP	Solid colorless, acicular crystal or white
Boiling Point	181.9°C at 760 mm
Melting Point	42.5 to 43°C
Specific Gravity	1.0576 at 20°C/4°C
Vapor Pressure	
at 25°C	0.530 mm
at 40°C	1 mm
Vapor Density (air=1)	3.24
Solubility	Soluble (86.6 gm/L of H_2O), infinitely soluble in hot H_2O
Log Partition Coefficient (octanol/H_2O)	1.48
Henry's Law Constant	

Source: SAI (1980).

Table 24.1-2

CHEMICAL DATA SUMMARY FOR 2-NITROPHENOL

Property	Value for 2-nitrophenol
CAS Registry No.	
Synonyms	o-nitrophenol
Molecular Weight	139.11
Molecular Formula	$NO_2C_6H_4OH$
Molecular Structure	
Physical State at STP	Light yellow needles or prisms
Boiling Point	214/217°C
Melting Point	45°C
Specific Gravity	
Vapor Pressure	20 mm @ 105°C, 100 mm @ 146°C
Vapor Density (air=1)	
Solubility	2.1 g/l @ 20°C, 10.8 g/l @ 100°C
Log Partition Coefficient (octanol/H_2O)	
Henry's Law Constant	

Source: SAI (1980).

Table 24.1-3

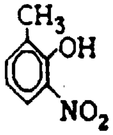
CHEMICAL DATA SUMMARY FOR 4-NITROPHENOL

Property	Value for 4-nitrophenol
CAS Registry No.	
Synonyms	p-nitrophenol
Molecular Weight	139.11
Molecular Formula	$NO_2C_6H_4OH$
Molecular Structure	
Physical State at STP	Colorless to yellowish crystals
Boiling Point	279°C (decomposes)
Melting Point	114°C
Specific Gravity	
Vapor Pressure	2.2 mm @ 146°C, 18.7 mm @ 186°C
Vapor Density (air=1)	
Solubility	16 g/l @ 25°C, 269 g/l @ 90°C
Log Partition Coefficient (octanol/H_2O)	
Henry's Law Constant	

Source: SAI (1980).

Table 24.1-4

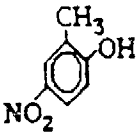
CHEMICAL DATA SUMMARY FOR 3-NITRO-2-HYDROXYTOLUENE

Property	Value for 3-Nitro-2-Hydroxytoluene
CAS Registry No.	
Synonyms	3-nitro-o-cresol
Molecular Weight	153.14
Molecular Formula	3-NO_2-2-$CH_3C_6H_3OH$
Molecular Structure	
Physical State at STP	Pale yellow crystals
Boiling Point	
Melting Point	147°C
Specific Gravity	
Vapor Pressure	
Vapor Density (air=1)	
Solubility	
Log Partition coefficient (octanol/H_2O)	
Henry's Law Constant	

Source: SAI (1980).

Table 24.1-5

CHEMICAL DATA SUMMARY FOR 5-NITRO-2-HYDROXYTOLUENE

Property	Value for 5-nitro-2-hydroxytoluene
CAS Registry No.	
Synonyms	5-nitro-o-cresol
Molecular Weight	153.14
Molecular Formula	
Molecular Structure	
Physical State at STP	Yellow crystals
Boiling Point	
Melting Point	118°C
Specific Gravity	
Vapor Pressure	
Vapor Density (air=1)	
Solubility	
Log Partition Coefficient (octanol/H_2O)	
Henry's Law Constant	

Source: SAI (1980).

24.3 INDIRECT PRODUCTION AND EMISSIONS IN CALIFORNIA

24.3.1 Emissions from Automobile Exhaust

A review of the literature on phenol emissions by Lesh and Mead (1985) identified one study which estimated emissions from automobile exhaust. This study, conducted by Arthur D. Little, Inc. (Scow et al., 1981), indicated that approximately 19 percent (2,280 MT/yr) of all phenol emissions occurred from this source. Lesh and Mead (1985), updating this earlier estimate on the basis of data quality, completeness and acquisition date, estimated that 1,880 MT of phenol are emitted annually.

We calculated California emissions of phenol from automobile exhaust by multiplying the national data by the 1982 ratio of California to U.S. vehicle miles traveled (MVMA, 1984):

California Emissions from Automobile Exhaust $= (0.107)(1.88 \times 10^9 \text{g})/(453.6 \text{ g/lb})$

$= 443{,}474$ lb/yr (222 tons/yr)

24.3.2 Emissions from Wood Burning

Lesh and Mead (1985) report phenol emissions from residential combustion of wood in wood stoves and fireplaces from two previous studies, based upon 1978 data. Their update of these earlier calculations estimated that 2,280 Mg/yr were emitted by wood burning sources. One method of estimating California emissions is to apportion the national estimate to California on the basis of population. Thus,

California Emissions from Wood Burning $= (0.11)(2.28 \times 10^9 \text{ g/yr})/(453.6 \text{ g/lb})$

$= 552{,}910$ lb/yr (276 tons/yr)

24.3.3 Emissions from Wastewater Treatment and Sludge Incineration

A recent review by the EPA has determined that the potential for volatilization of phenol from wastewater treatment plants is negligible (USEPA, 1986). Although phenol is present in most wastewater treatment plant sludges (Frick and Clarkson, 1984), it is unlikely to be present in emissions from sludge incineration.

24.4 INDUSTRIAL USE AND EMISSIONS

Most phenol is used as a chemical intermediate in the production of other organic chemicals. In 1984 approximately 45 percent of the compound was used to produce phenolic resins. Another 25 percent was used in the manufacture of bisphenol-A, while 15 percent was used to produce caprolactam. The remainder of phenol was used as an intermediate in the production of adipic acid, nonylphenol, dodecylphenol, salicylic acid, and pentachlorophenol. With the exception of phenolic resins, none of these compounds are produced in California (Lesh and Mead, 1985). Phenolic resins are produced at 90 to 125 plants in the U.S.

We have identified seven phenol-formaldehyde resin manufacturing plants in California. Other facilities in the state may not have been located, although it is not likely that many have been omitted, since there are no more than 24 such plants located in the entire Pacific region (SAI, 1980). The seven facilities we found are operated by Borden Inc. in Fremont; Cargill, Inc. in Lynwood; Georgia-Pacific Corp. in Elk Grove and Ukiah; United Technologies/Inmont Corp. in Anaheim; Monsanto Co. in Santa Clara; Reichhold Chemicals, Inc. in South San Francisco; and Rohm and Haas California, Inc. in Redwood City (Rogozen et al., 1984; Newby, 1986).

Although we do not have production data for each of these plants, we can estimate total phenol emissions from all seven sites by using typical plant emissions. Approximately 4,180 lb phenol per year were reported for a typical resin manufacturing site (SAI, 1980). Thus, about 29,260 lb/yr (14.6

tons/yr) of phenol are emitted by phenol-formaldehyde manufacturing within California.

One further industrial use of phenol in the state takes place at the Chevron U.S.A. refinery, where phenol is used as an extraction solvent in lube oil treatment (Williams, 1986).

Table 24.4-1 identifies point sources of phenol, which are listed in the emission inventory of the Bay Area Air Quality Management District (Hill, 1985). Approximately 16.7 tons/yr are emitted by these sources.

24.5 CONSUMER USE AND EMISSIONS

In 1980, 94.6 percent of phenol production was used as an intermediate in the manufacture of other chemicals, with only 5.4 percent used for other products. The only consumer use identified thus far is as an ingredient of certain brands of throat lozenges. The amount of phenol emitted by such sources is likely to be quite small.

24.6 EMISSION SUMMARY

Only one phenol producing facility exists in California, in Santa Fe Springs. Emissions from this plant are approximately 1.2 tons/yr. We estimate that 222 tons/yr are a component of automobile exhaust, while wood combustion emissions are 276 tons. The only industrial use for phenol in the state is the production of phenol-formaldehyde resins by at least 7 facilities. We estimate that 15 tons of phenol are released annually from these sites. Total California phenol emissions are, therefore, approximately 514 tons/yr.

Table 24.4-1
PHENOL EMISSIONS IN THE SAN FRANCISCO BAY AREA

Source	City	Emissions (tons/yr)
Alameda County		
Able Auto Body		T
American Brass and Iron		T
Borden Chemical Co.	Fremont	T
California Florida Plant	Fremont	T
Clorox Technical Center	Pleasanton	U
DOE-Sandia National Laboratory	Livermore	T
Drew Refining Company	Berkeley	T
Hexcel Livermore Plant	Livermore	T
Intel Corporation	Livermore & Santa Clara	T
Kaiser Aerotech	San Leandro	T
Kaiser Aluminum & Chemical	Pleasanton	T
Lawrence Livermore National Laboratory	Livermore	T
Macaulay Foundry, Inc.	Berkeley	0.2
National Airmotive Corporation	Oakland	T
Naval Air Station Alameda	Alameda	U
Pacific Steel Casting Co.	Berkeley	0.1
Peterbilt Motors Co.	Newark	T
Prescolite, Div. of U.S.I.	San Leandro	T
Segundo Tool & Mfg, Inc.	Union City	T
Transamerica Delaval Inc.	Oakland	T
U S Veterans Administration	Livermore	T
United Can Company	Hayward	T
United States Pipe & Foundry	Union City	T
Washington Hospital	Fremont	T
World Airways, Inc.	Oakland	U
Contra Costa		
California & Hawaiian Sugar	Crockett	T
Central Contra Costa Sanitation District	Martinez	T
Chevron Research Company	Richmond	T
Crown Zellerbach Corp.	Antioch	U
Delta Diablo Sanitation	Antioch	T
Great Western Chemical Co.	Richmond	T
IT Corporation, Oil Repr.	Martinez	U
IT Corporation, Vine Hil.	Martinez	U
Shell Oil Company	Martinez	U
US Steel Corp.	Pittsburg	1.8
Union Chemicals	Rodeo	T

Table 24.4-1 (Continued)

Source	City	Emissions (tons/yr)
Union Oil Company	Rodeo	2.0
West Contra Costa Sanitation District	Richmond	T
Marin		
Central Marin Sanitation District	San Rafael	T
San Francisco		
Best Foods	San Francisco	T
Mount Zion Hospital & Me.	San Francisco	T
Pacific Gas & Electric Co.	San Francisco	T
Todd Shipyards Corporation	San Francisco	0.2
US Army, Presidio of San Francisco	San Francisco	T
San Mateo		
Ampex Corporation		T
Genentech, Inc.	South San Francisco	T
SRI International	Menlo Park	T
San Mateo City of Sewage	San Mateo	T
United Airlines, Maintenance	South San Francisco	4.6
Santa Clara		
Advanced Micro Devices		U
American Microsystems		0.5
Beckman Instruments, Inc.	Palo Alto	T
Burke Industries, Inc.	San Jose	U
Data General Corporation	Sunnyvale	T
Dysan Corporation	Santa Clara	T
Fairchild Camera and Instruments	San Jose	0.5
Ford Aerospace & Communications	Palo Alto	T
General Electric Co.	San Jose	0.1
Harold Doc May Subregion	Palo Alto	T
Hewlett-Packard Co, Opto.	Palo Alto	0.1
Hewlett-Packard Company	Palo Alto	0.8
Hewlett-Packard Co, Stan.	Palo Alto	T
Hewlett-Packard Co, Pers.	Sunnyvale	U
Hewlett-Packard Co, Santa Clara	Santa Clara	0.2
Lockheed Missiles & Space	Sunnyvale	U
Magnetic Peripherals, Inc.	Cupertino	0.1
Monolithic Memories, Inc.	Sunnyvale	2.4
National Semiconductor Co.	Santa Clara	U
Owens-Corning Fiberglass	Santa Clara	T

Table 24.4-1 (Continued)

Source	City	Emissions (tons/yr)
Precision Monolithics	Santa Clara	U
Santa Clara Valley Medical	San Jose	T
Siemens Optoelectronics	Cupertino	0.5
Signetics Corporation	Sunnyvale	2.7
Siliconix, Incorporated	Santa Clara	U
Syntex (USA) Inc.	Palo Alto	T
TRW Microwave Inc.	Sunnyvale	U
Van Waters & Rogers	San Jose	T
Varian Associates, Corporation	Palo Alto	T
Veterans Administration	Palo Alto	T
Watkins-Johnson Company	Palo Alto	T
Western Spray Painting	Santa Clara	U
Solano		
Exxon Company USA	Benicia	T
Exxon Corporation	Benicia	U
Mare Island Naval Shipyards	Vallejo	U
Travis AFB	Travis AFB	T
Sonoma		
Hewlett-Packard Co.	Santa Rosa	T
Hewlett-Packard Company	Santa Rosa	T

Source: Bay Area Air Quality Management District (Hill, 1985).

[a] T = 0-0.1 tons/yr; U = Phenol is handled but emissions cannot be estimated from available information.

24.7 SUMMARY OF AMBIENT CONCENTRATION DATA

24.7.1 Gas Phase Concentrations

There are essentially no data for gas phase phenol and nitrophenols in California air. Pellizzari (1979) measured up to 87 ppb of phenol (mean value 17 ppb) in Upland, CA, in the vicinity of a phenolic resin factory. Similar values were obtained near industrial sources at several locations in the U.S., e.g. up to 420 ppb (mean 78 ppb) in El Paso, TX (Pellizzari, 1979).

Urban values are limited to the data of Leuenberger et al. (1985) for Portland, OR; of Kuwata et al. (1980) for Osaka, Japan; and of Hoshika and Muto (1978) for Nagoya, Japan. Results of these studies are summarized in Table 24.7-1. Urban levels of phenols in California are probably similar, i.e. up to 1-3 ppb.

24.7.2 Condensed Phase Concentrations

Phenols are polar, soluble molecules with high Henry's law coefficients, and are expected to be efficiently scavenged from the gas phase by rain and fog. Nojima et al. (1976) first reported on several nitrophenols in rainwater. The study of Leuenberger et al. (1985) included simultaneous measurements of gas phase, aerosol phase and rainwater phenols in Portland, OR (aerosol concentrations of phenols were negligible). Kawamura and Kaplan (1983, 1986) measured several phenols in Los Angeles rainwater. Results of these studies are summarized in Table 24.7-2. With typical concentrations of 2-10 μg/L, phenols are among the most abundant organic compounds in rainwater.

24.8 ATMOSPHERIC CHEMISTRY

24.8.1 In-Situ Formation

Phenol and the nitrophenols under review in this chapter may form in the atmosphere by gas phase as well as liquid phase reactions involving

Table 24.7-1

GAS PHASE CONCENTRATIONS OF PHENOLS

(Concentrations in ppb)

			Concentration		
Sample Type	Location	Compound	Mean	Max	Reference
Near source	Upland, CA	phenol	17	87	Pellizzari, 1979
	El Paso, TX	phenol	78	420	Pellizzari, 1979
	Other U.S. locations	phenol	50	200	Pellizzari, 1979
	Nagoya, Japan	phenol	50	-	Hoshika and Muto, 1978
Urban	Nagoya, Japan	phenol	0.44	2.3	Hoshika and Muto, 1978
	Osaka, Japan	phenol	0.55	1.0	Kuwata et al., 1980
	Portland, OR	phenol	0.1	0.2	Leuenberger et al., 1985
		2-nitrophenol	0.004	0.01	

[a] During rain events; other gas phase phenols measured included o-, m-, and p-cresol (see Chapter 11), five dimethylphenols, methoxyphenol, and several di, tri and tetrachlorophenols.

Table 24.7-2

PHENOLS IN RAINWATER

Location	Compound[a]	Concentration (μg/L)	Reference
Yokohama, Japan	4-nitrophenol	b	Nojima et al., 1976
	2-methyl-6-nitrophenol	b	
	2-methyl-4-nitrophenol	b	
Los Angeles, CA	phenol	c	Kawamura and Kaplan, 1983
	2-nitrophenol	c	
	4-bromophenol	c	
	3,4,5-trimethylphenol	c	
Portland, OR	phenol	>0.28	Leuenberger et al., 1985
	2-methylphenol	>1.0	
	3- and 4-methylphenol	>1.1	
	2-methoxyphenol	>2.1	
	2,6-dimethylphenol	0.14	
	2-nitrophenol	0.06	
	2,4- and 2,5-dimethylphenol	0.82	
	2,4-dichlorophenol	0.006	
	3,5-dimethylphenol	0.49	
	3,4-dimethylphenol	0.13	
	2,6-dichlorophenol	1.3×10^{-3}	
	2,4,6-trichlorophenol	1.4×10^{-3}	
	2,4,5-trichlorophenol	1.1×10^{-3}	
	2,3,4,6-tetrachlorophenol	0.020	
	pentachlorophenol	0.054	
Los Angeles, CA	phenol	up to 8	Kawamura and Kaplan, 1986
	2-methylphenol	up to 2	
	4-methylphenol	up to 5	
	2-nitrophenol	up to 1	
	4-methyl-3-nitrophenol	up to 4	

---

[a] Compounds reviewed in this chapter are underlined.

[b] Identified, concentration not reported.

[c] Individual concentrations not reported, sum of phenols = 2-8 μg/L.

alkylbenzenes and styrenes. Unfortunately, the importance of these reactions in urban air has not yet been assessed by direct field measurements: only laboratory studies of reaction kinetics and products are available, These studies indicate that the following reactions will produce phenols in air:

- Phenol: reaction of OH with benzene

- Nitrophenols (2- and 4-nitro):
    - Reaction of OH with phenol and with nitrobenzene;
    - Reaction of NO_3 with phenol; and
    - Thermal decomposition of peroxybenzoyl nitrate (PBzN).

- Nitrocresols (3-NO_2 and 5-NO_2-o-cresol):
    - Reaction of OH with cresols and with nitrotoluenes; and
    - Reaction of NO_3 with cresols.

- Dinitrocresols (2,4-dinitro cresol):
    - Reaction of OH with nitrocresols and dinitrotoluenes; and
    - Reaction of NO_3 with nitrocresols.

These reactions are outlined below for each compound under review in this chapter. The structures of these compouunds are given in Figure 24.8-1. Kinetic data relevant to their reactions are listed in Table 24.8-1.

24.8.1.1 Phenol

Phenol is a major product of the reaction of OH with benzene in the gas phase (e.g. Bandow et al., 1985) and in water (NAS, 1980). The gas phase reaction is slow. Phenol is the major reaction product, followed by nitrobenzene and ring-opening products such as glyoxal (Bandow et al., 1985). The aqueous phase reaction of OH with benzene is also slow, with phenol and hydroxymucondialdehyde as major products (NAS, 1980). The overall mechanisms for these reactions are summarized in Figure 24.8-2.

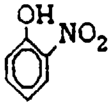
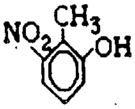
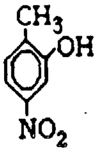
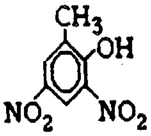
Structure	Name	Alternate Names
	Phenol	---
	2-nitrophenol	O-nitrophenol
	4-nitrophenol	P-nitrophenol
	2-methyl-3-nitrophenol	3-nitro-o-cresol 2-hydroxy-6-nitrotoluene
	2-methyl-5-nitrophenol	5-nitro-o-cresol 2-hydroxy-4-nitrotoluene
	2-methyl-4,6-dinitrophenol	2,4-dinitro-o-cresol 2-hydroxy-3,5-dinitrophenol 6-methyl,2-4,dinitrophenol

Figure 24.8-1. Structures of Selected Phenols.

Table 24.8-1

KINETIC DATA FOR ATMOSPHERIC FORMATION AND REMOVAL OF PHENOLS BY GAS PHASE REACTIONS

	Formation		Removal		
Compound[a]	Reaction[b] of	Rate Constant,[c] $cm^3 molecule^{-1} sec^{-1}$	Reaction[b] With		Rate Constant,[c] $cm^3 molecule^{-1} sec^{-1}$
<u>Phenol</u>	Benzene + OH	1.2×10^{-12}	OH		2×10^{-11}[d]
			NO_3		2.1×10^{-12}
<u>Nitrophenols</u>	Phenol + OH	$2. \times 10^{-11}$[d]	OH	2-nitro	2.3×10^{-11}[d]
(2-nitrophenol and 4-nitrophenol)	Nitrobenzene + OH	1.3×10^{-13}		4-nitro	3.4×10^{-13}[d]
	Benzaldehyde + OH[e]	1.3×10^{-11}			
	Phenol + NO_3	2.1×10^{-12}	NO_3		no data
<u>Nitrocresols</u>	Cresols + OH ortho	4.7×10^{-11}	OH	3-nitro	2.3×10^{-13}[d]
(2-methyl-3-nitrophenol and 2-methyl-5-nitrophenol)	meta	6.7×10^{-11}		5-nitro	3.4×10^{-13}[d]
	para	5.2×10^{-11}			
	Nitrotoluenes + OH ortho	0.9×10^{-11}[f]			
	meta	0.32×10^{-11}[f]			
	para	0.38×10^{-11}[f]			
	Cresols + NO_3 ortho	1.2×10^{-11}	NO_3		no data
	meta	0.9×10^{-11}			
	para	1.3×10^{-11}			

Table 24.8-1 (Continued)

	Formation		Removal	
Compound[a]	Reaction[b] of	Rate Constant,[c] $cm^3 molecule^{-1} sec^{-1}$	Reaction[b] With	Rate Constant,[c] $cm^3 molecule^{-1} sec^{-1}$
Dinitrocresols (2-methyl-4, 6-dinitro phenol)	Nitrocresols + OH	no data	OH	3.0×10^{-14}[d]
	Dinitrotoluenes + OH	no data		
	Nitrocresols + NO_3	no data	NO_3	no data

---

[a] See structures in Figure 24.8-1.

[b] Initial reaction, followed by pathways shown in Figures 24.8-2 to 24.8-8.

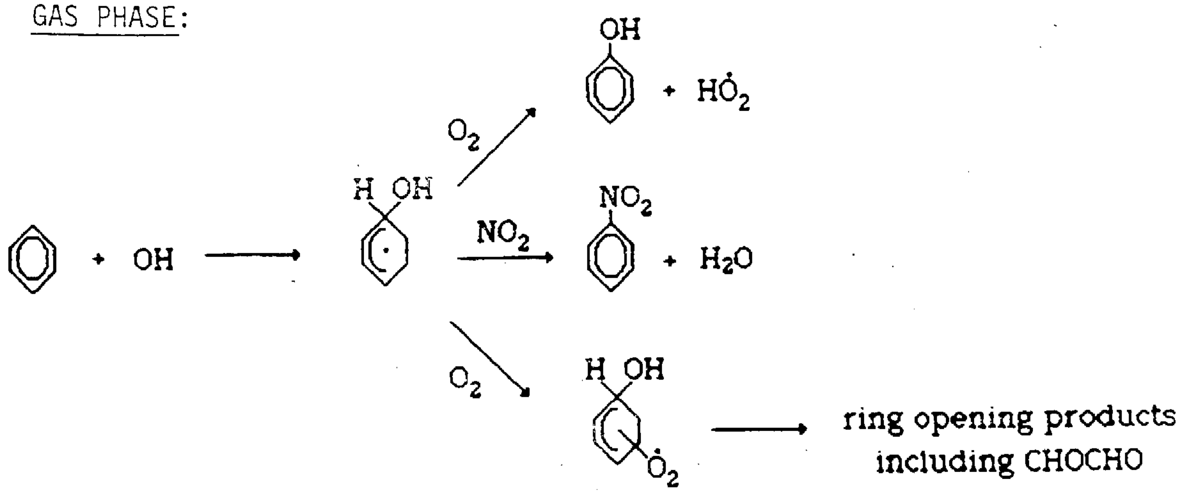
[c] From Chapter 3 and references therein.

[d] Estimated from structure-reactivity relationships; see Chapter 3.

[e] Benzaldehyde + OH → PBzN → thermal decomposition; see text.

[f] From data of O'Brien et al. (1978) relative to toluene and placed on an absolute basis using k_{OH} + toluene = 6.4×10^{-12} cm^3 $molecule^{-1}$ sec^{-1}.

GAS PHASE:



AQUEOUS PHASE:

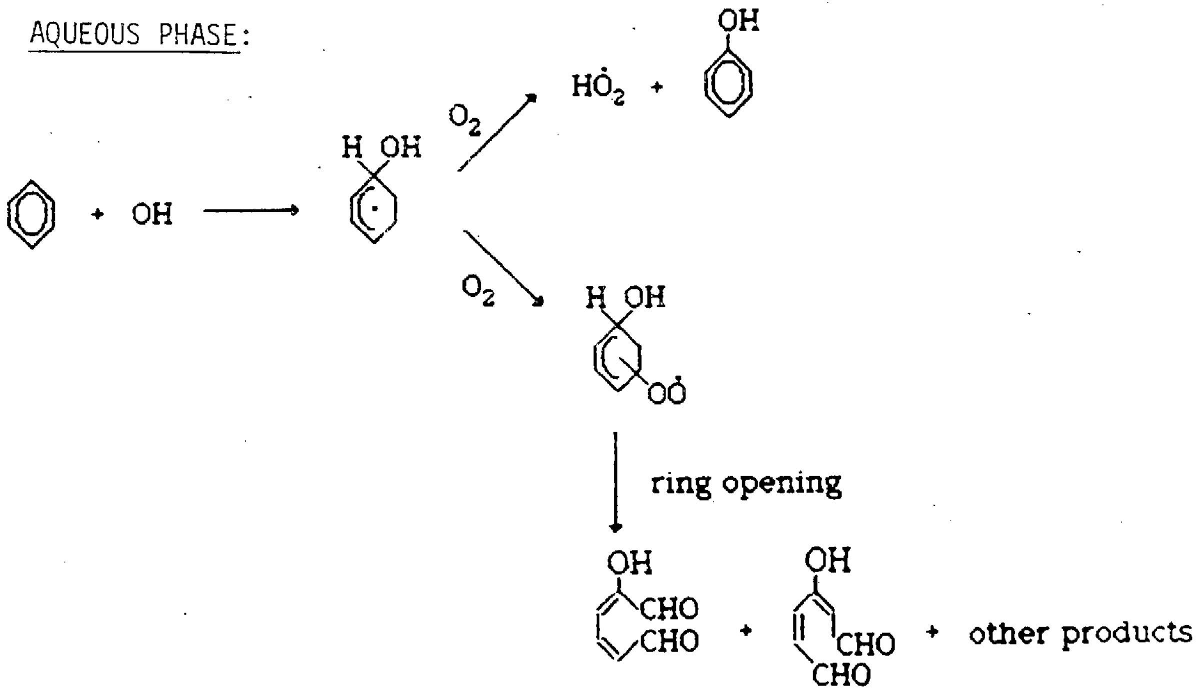


Figure 24.8-2. OH-Benzene Reaction.

24.8.1.2 Nitrophenols

The reaction of phenol with OH yields 2-nitrophenol and 4-nitrophenol in the gas phase, along with other products. This reaction has not been studied experimentally. A plausible mechanism, based upon that proposed by Grosjean (1984, 1985) for cresols (see details in Chapter 11, Section 11.8), is summarized in Figure 24.8-3. OH addition is expected to be the major pathway at ambient temperature, and abstraction is expected to involve the H atom from the weak phenolic O-H bond. The OH adduct may react with NO_2 to form nitrophenols and with O_2 (addition) to yield ring-opening dicarbonyl products, including glyoxal (CHOCHO) and glyoxylic acid (CHOCOOH). The relative importance of these two pathways is not known. The phenoxy radical (OH abstraction pathway) is expected to react with NO_2 to form nitrophenols. The rate constant for the OH-phenol reaction has not been measured; a value of about 2×10^{-11} cm^3 $molecule^{-1}$ sec^{-1} has been estimated from structure-reactivity relationships (see Chapter 3).

The reaction of OH with nitrobenzene also yields nitrophenols. The mechanism of this reaction has been discussed detail in Section 22.8 (see Figure 22.8-2). However, this reaction is slow, $k_{OH} \sim 1.3 \times 10^{-13}$ cm^3 $molecule^{-1}$ sec^{-1}, and will not be a major source of nitrophenols in the atmosphere.

The third reaction of interest is that of phenol with the nitrate radical. Kinetic data for the reaction of NO_3 with phenols are available for phenol and for o-, m-, and p-cresol (Carter et al., 1981). Product studies are not available. The reaction is expected to proceed by H-atom abstraction from the weak phenolic OH bond, leading to the phenoxy radical:

$$C_6H_5OH + NO_3 \rightarrow HNO_3 + C_6H_5\overset{\circ}{O}$$

The phenoxy radical then reacts with NO_2 to form 2-nitrophenol and 4-nitrophenol as has been shown in Figure 24.8-3 for the OH-phenol abstraction pathway.

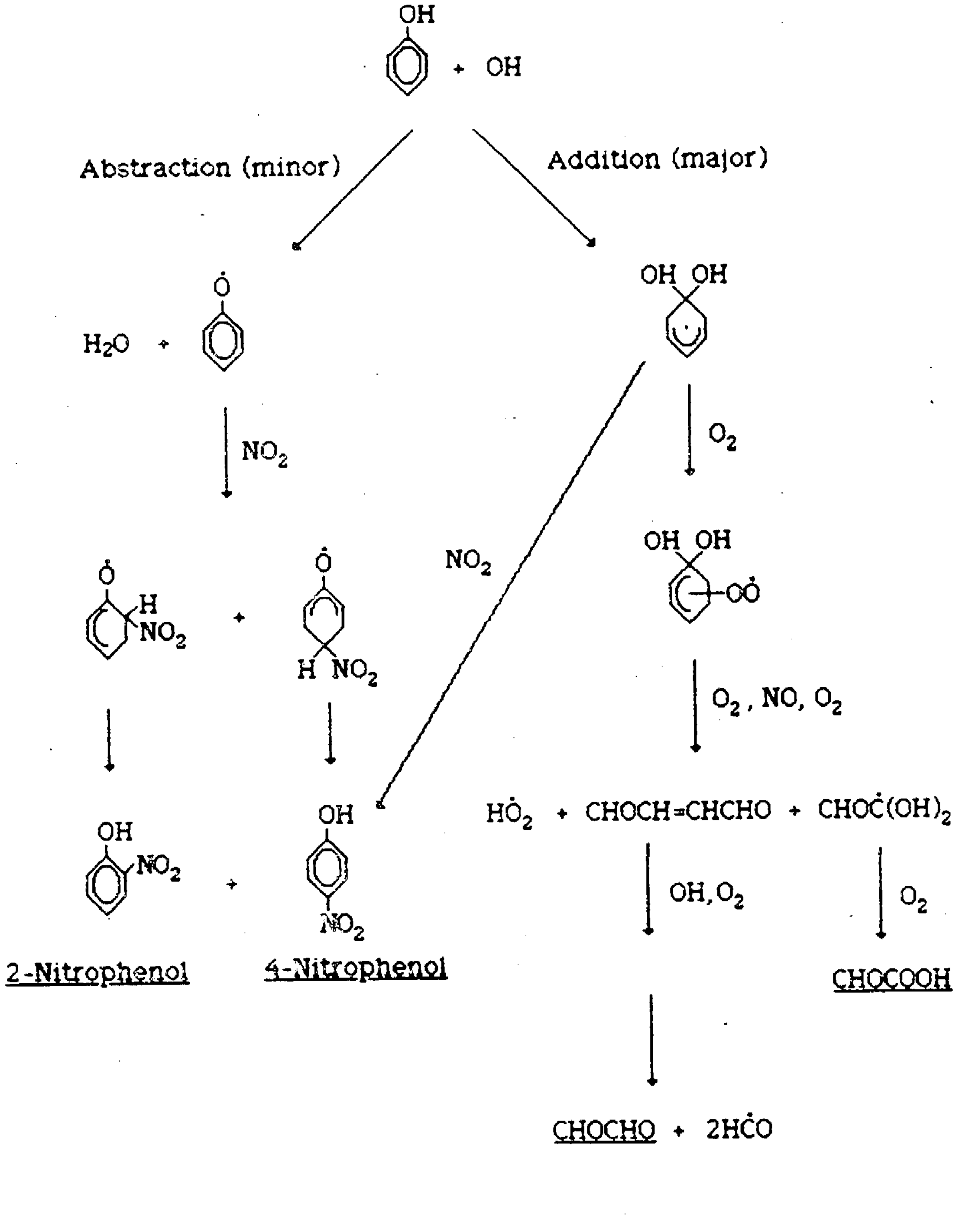


Figure 24.8-3. OH-Phenol Reaction.

The fourth reaction of interest is that involving the thermal decomposition of peroxybenzoyl nitrate, PBzN (Niki et al., 1979; Ohta and Mizoguchi, 1981; Grosjean, 1985b). The mechanism of this reaction is shown in Figure 24.8-4 and involves the steps of reaction of $C_6H_5CO_3$ with NO to form $C_6H_5CO_2$, unimolecular decomposition of $C_6H_5CO_2$ into CO_2 and C_6H_5, reactions of the phenyl radical with O_2 and NO to form the phenoxy radical, and finally reaction of the phenoxy radical with NO_2 to form nitrophenols. In the atmosphere, the precursor of PBzN is benzaldehyde (Figure 24.8-5) which in turn may be present as a result of (1) direct emissions; (2) reaction of toluene with OH (the abstraction pathway, about 10 percent of the overall toluene-OH reaction); and (3) reaction of styrenes with OH and with ozone, both yielding benzaldehyde as major product (Grosjean, 1985b).

24.8.1.3 Nitrocresols

The reactions of cresols with OH and with NO_3 lead to nitrocresols. These reactions have been discussed in detail in Section 11.8. A summary of the corresponding reaction pathways is given in Figure 24.8-6. Rate constants are available for the reactions of all three cresol isomers with OH (Perry et al., 1977; Atkinson et al., 1978) and with NO_3 (Carter et al., 1981). These two reactions constitute major pathways for cresol removal and for nitrocresol formation in the atmosphere.

Nitrocresols may also form by reaction of OH with nitrotoluenes. This reaction has not been studied experimentally, and a tentative reaction mechanism is given in Figure 24.8-7 using the m-nitrotoluene isomer as an example (this isomer is the major nitrotoluene produced in the toluene-OH reaction). The expected products are nitrobenzaldehyde (OH abstraction pathway, minor), dinitrotoluenes, nitrocresols, and ring-opening products including dicarbonyls and nitro-substituted carbonyls. Rate constants for the nitrotoluene-OH reactions have not been measured, but rates relative to that of the OH-toluene reaction have been reported by O'Brien et al. (1978). Using a rate constant of 0.64×10^{-11} cm^3 $molecule^{-1}$ sec^{-1} for the OH-toluene reaction leads to nitrotoluene-OH reaction rate constants of $0.3\text{-}0.9 \times 10^{-11}$ cm^3 $molecule^{-1}$ sec^{-1} (Table 24.8-1). These rate constants are 5 to 20 percent of those for the OH-cresols reactions.

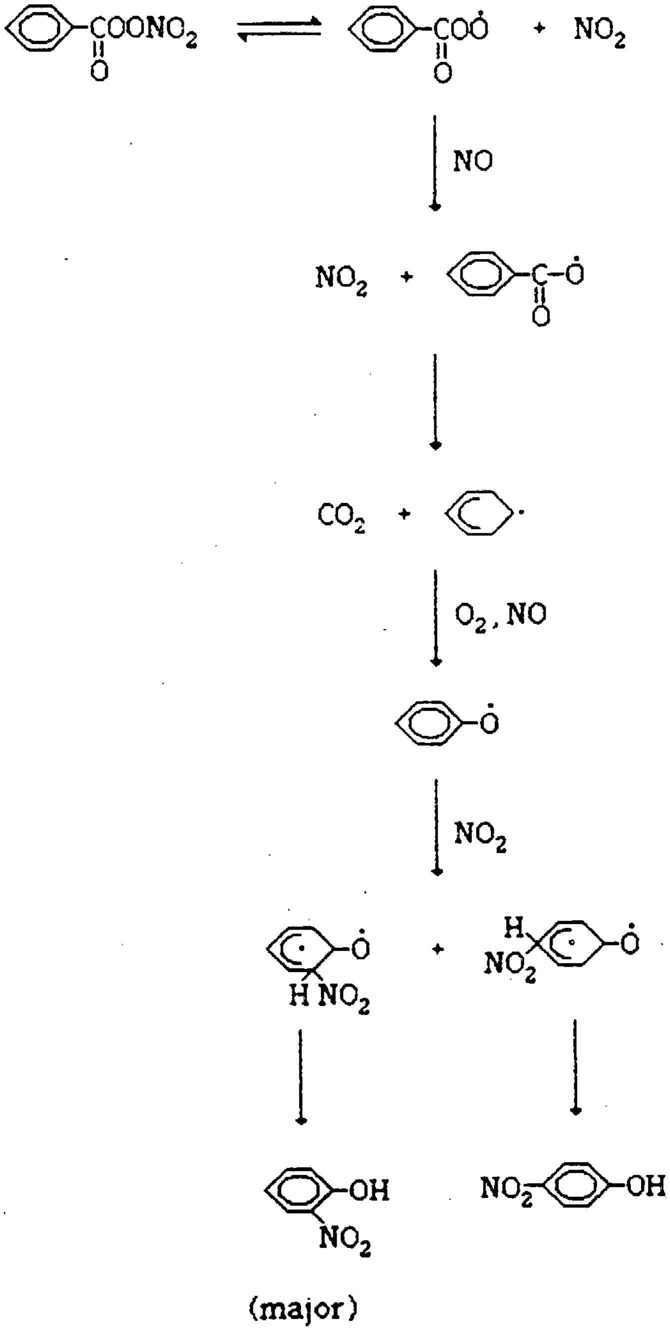


Figure 24.8-4. Thermal Decomposition of PBzN (adopted from Grosjean, 1985b).

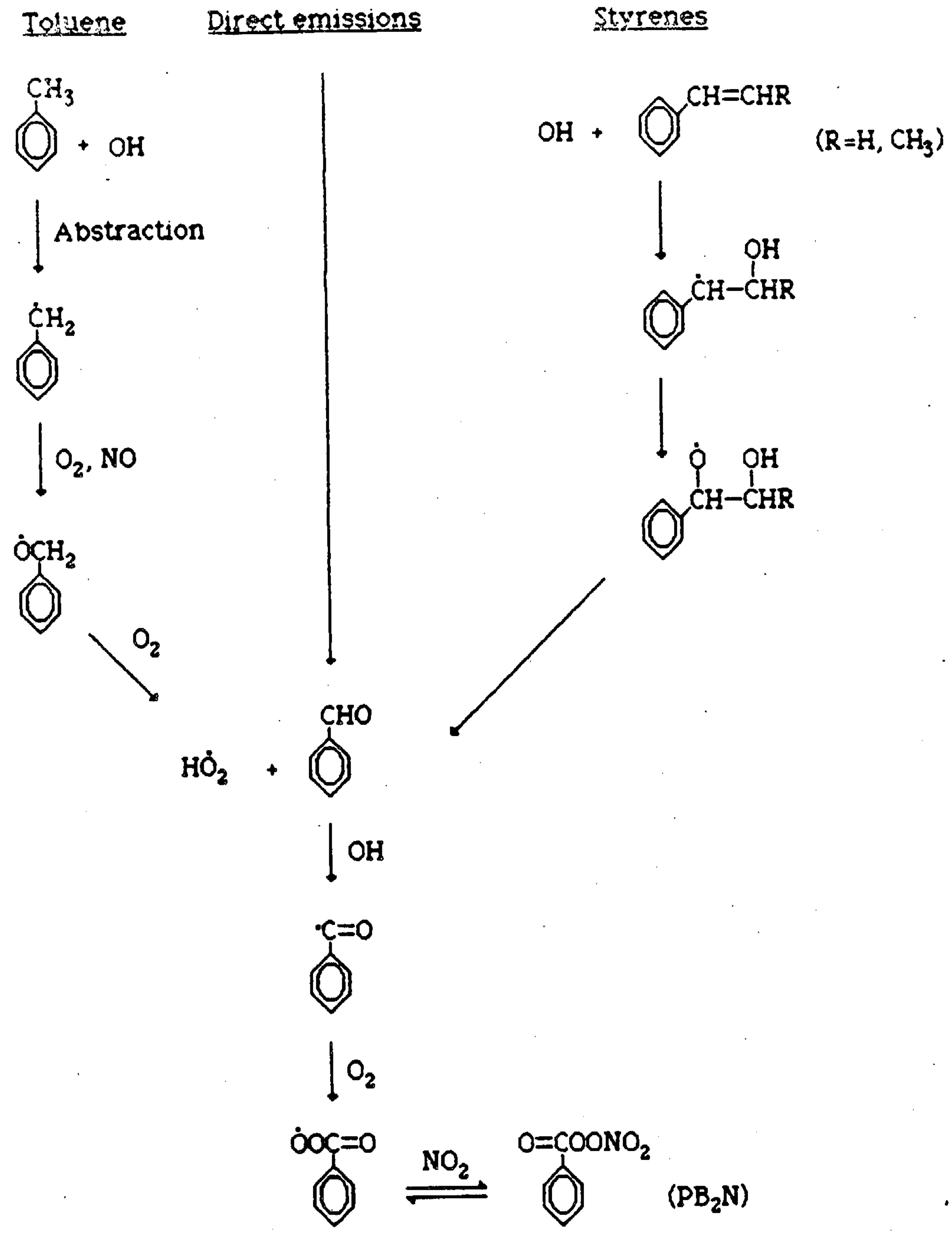


Figure 24.8-5. PBzN and its Precursors (adopted from Grosjean, 1985b).

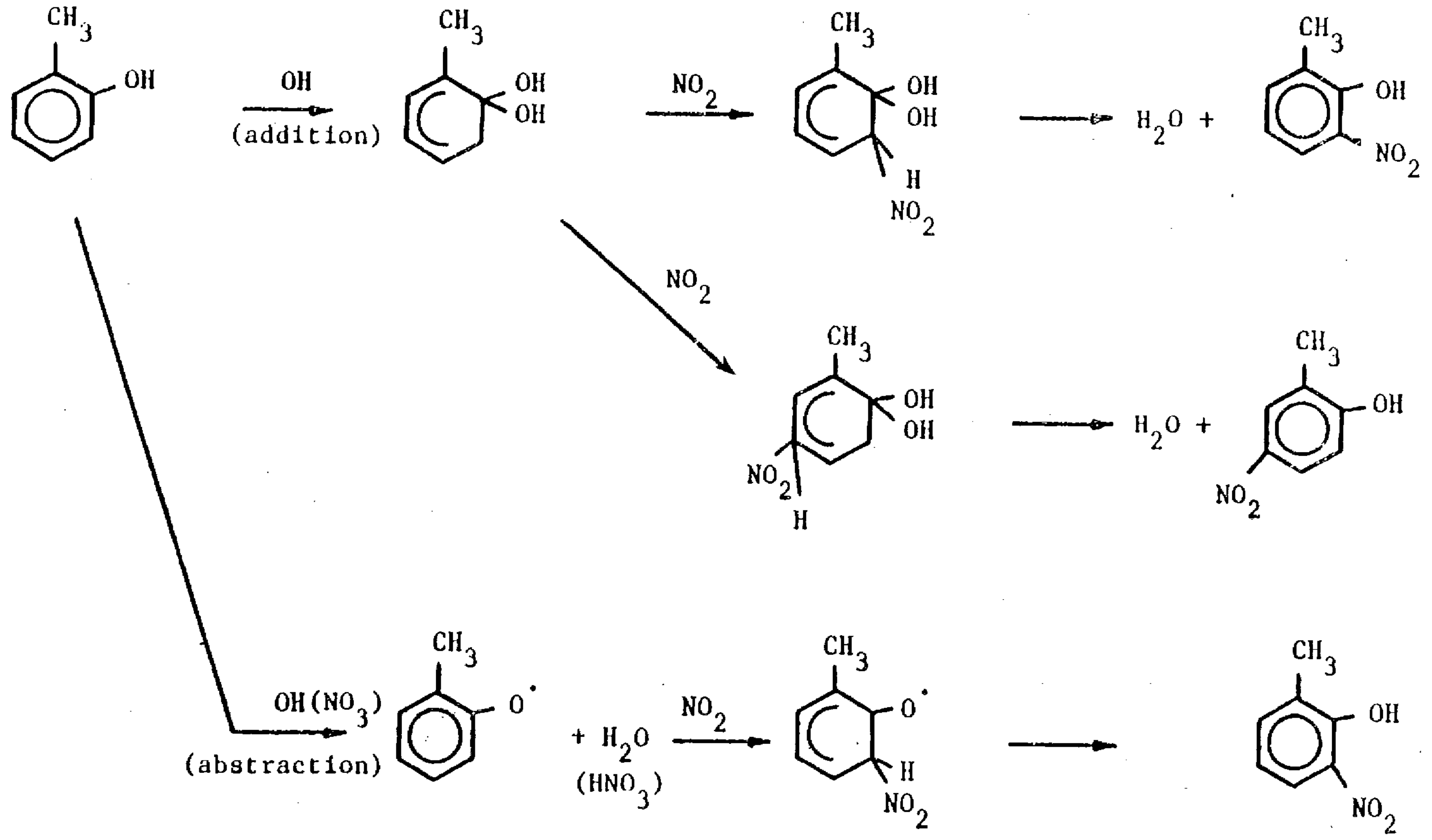


Figure 24.8-6. Reaction of NO_2 With Phenoxy Radical (Grosjean, 1984).

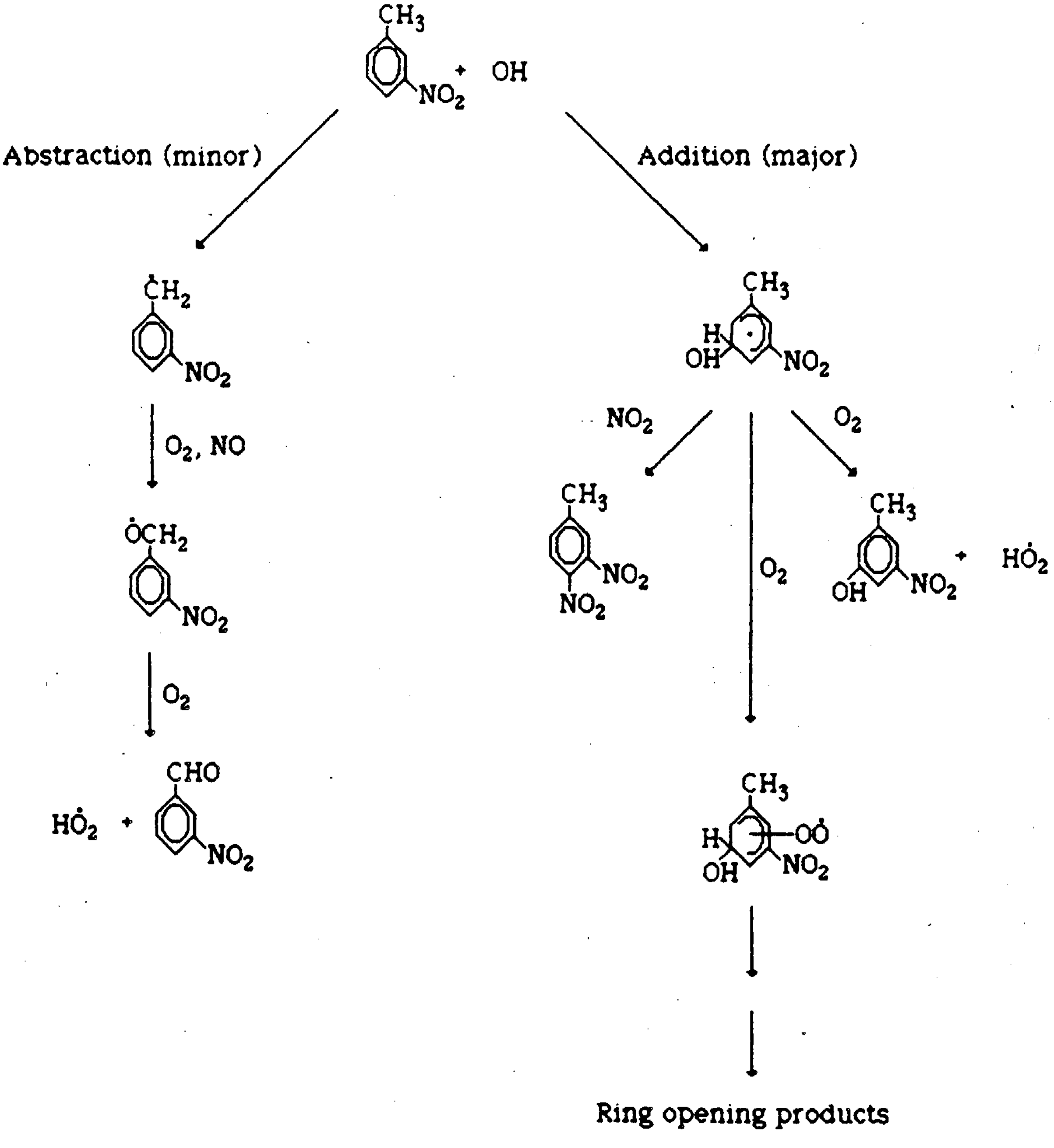


Figure 24.8-7. OH-Nitrotoluene Reaction.

24.8.1.4 Dinitrocresols

The atmospheric formation pathways of dinitrocresols are identical to those discussed above for nitrocresols, i.e. reaction of OH with dinitrotoluenes. No rate constants are available for these reactions. Values estimated from structure-reactivity relationships are given in Table 24.8-1. Dinitrocresol formation initiated by reaction of OH and NO_3 with nitrocresol has been studied experimentally by Grosjean (1984, 1985a) for one nitrocresol isomer, 4-hydroxy-3-nitrotoluene. The corresponding reaction pathways are shown in Figure 24.8-8. Dinitrocresol formation from dinitrotoluene is expected to be identical to that shown in Figure 24.8-7 for the OH-nitrotoluene reaction.

24.8.2 Removal Processes

All phenols are expected to be removed from the atmosphere by their reactions with OH and with NO_3. The corresponding rate constants have been listed earlier in Table 24.8-1. Many of these rate constants are values estimated from structure-reactivity relationships. Reaction mechanisms have been discussed in the preceding section of this chapter for most compounds since formation and removal processes of phenol, nitrophenols, nitrocresols and dinitrocresols are closely related. The focus of the following paragraphs is on the relative importance of in-situ formation and removal processes and the expected "net" result for each compound.

24.8.2.1 Phenol

The OH-phenol reaction mechanism has been described in Figure 24.8-3. The NO_3-phenol reaction mechanism is identical to that for the OH-phenol abstraction pathway shown in Figure 24.8-3. For any given OH concentration, phenol removal will be about 20 times faster than its production from benzene (k_{OH} + phenol/k_{OH} + benzene = $2 \times 10^{-11}/0.12 \times 10^{-11} = 16.7$). In the same way, phenol is rapidly removed by reaction with NO_3, while no reaction involving NO_3 is known to produce phenol. Overall, phenol is expected to be rapidly removed from urban air.

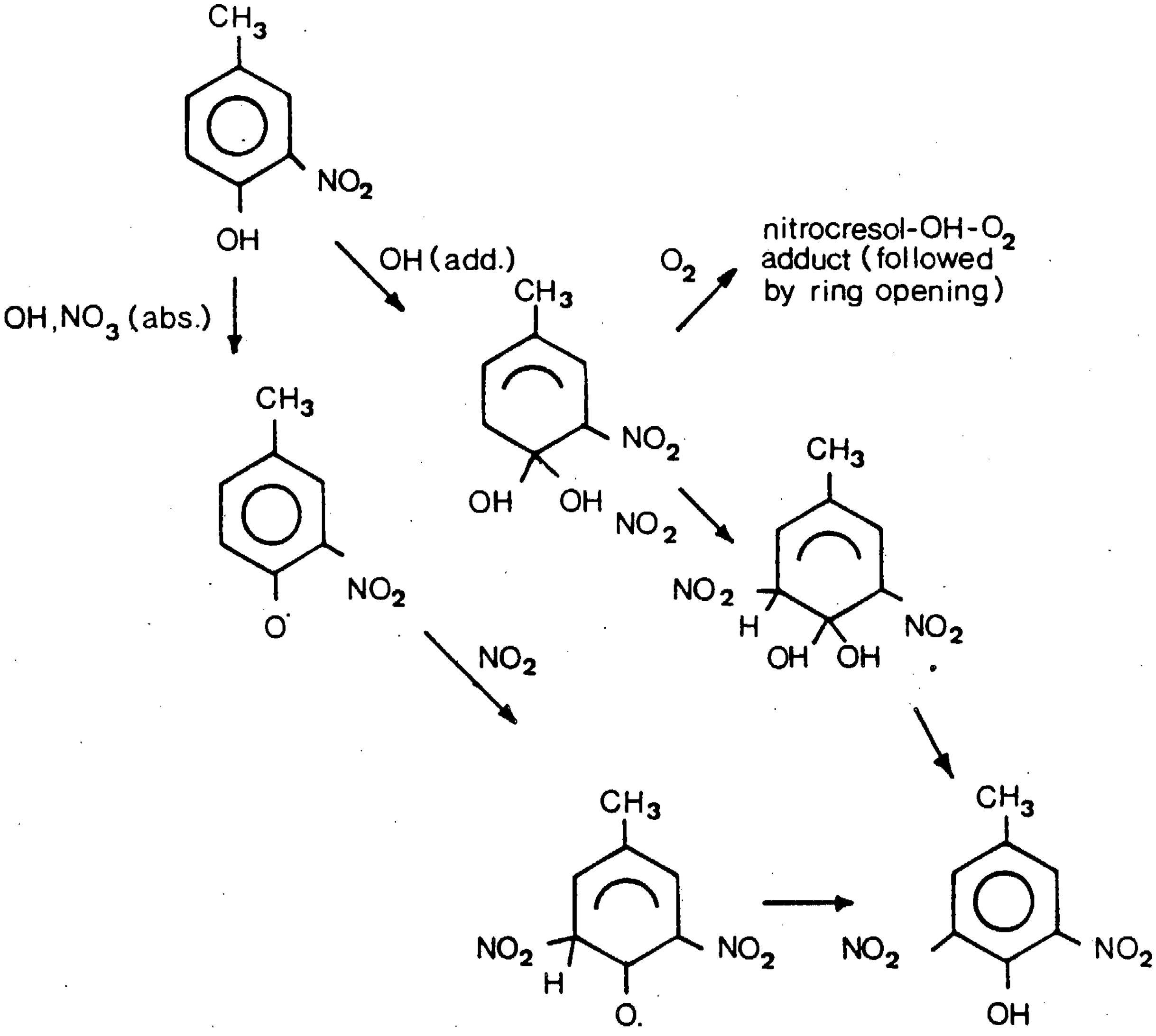


Figure 24.8-8. Formation of Dinitrocresols From Nitrocresols (Grosjean, 1985a).

24.8.2.2 Nitrophenols

Mechanisms for nitrophenol removal by reactions with OH and with NO_3 are expected to be identical to those shown in Figure 24.8-8 for nitrocresols, i.e. they would lead to dinitrophenols and ring-opening products. The nitro functional group decreases the reactivity of aromatic compounds towards electrophiles, hence nitrophenols are expected to be somewhat less reactive than phenols towards OH and NO_3. This is borne out by available kinetic data summarized in Table 24.8-3. A net production is therefore expected for 2-nitrophenol and 4-nitrophenol in the atmosphere.

24.8.2.3 Nitrocresols

Mechanisms for removal of nitrocresols by reaction with OH and with NO_3 have been described in Figure 24.8-8. No kinetic data are available for these reactions. Estimated values given in Table 24.8-1 show that nitrocresol removal by reaction with OH is much slower than nitrocresol formation from OH-cresols and OH-nitrotoluene reactions. A net production is thus expected for 2-methyl-3-nitrophenol and 2-methyl-5-nitrophenol in the daytime atmosphere (OH chemistry). The corresponding NO_3 chemistry is unclear due to lack of kinetic data. If the nitrocresol-NO_3 reactions are as fast as the cresol-NO_3 reactions, removal will offset production, thus resulting in a "zero" term for NO_3 chemistry. If the expected decrease in reactivity from the nitro group applies to the NO_3-nitrocresol reaction, this reaction will be slower than the NO_3-cresol reaction and the overall result will be a net production of nitrocresols via NO_3 chemistry.

24.8.2.4 Dinitrocresols

No kinetic data are available for the reactions of dinitrocresols with OH and NO_3. With two nitro groups, these compounds are expected to react only slowly with OH and NO_3, resulting in a net in-situ production in the atmosphere. Furthermore, dinitrocresols have high melting points, low vapor pressures, and condense as aerosols in laboratory studies (Grosjean 1984, 1985a) and presumably in the atmosphere as well. Condensation as aerosols would obviously "protect" dinitrocresols against gas phase removal processes including reactions with OH and NO_3. Particle scavenging by rain and fog and dry deposition would then become their dominant loss processes in the atmosphere.

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25.0

EVALUATION OF PHOSGENE

25.1 PHYSICAL AND CHEMICAL PROPERTIES

Table 25.1-1 summarizes the physical and chemical properties of phosgene.

25.2 DIRECT PRODUCTION IN CALIFORNIA

A recent study for the U.S. Environmental Protection Agency identified 16 plants where phosgene is produced (Lesh and Mead, 1985). No phosgene is manufactured in California.

25.3 INDIRECT PRODUCTION IN CALIFORNIA

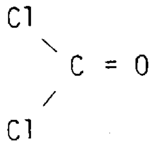
In-situ formation is believed to be the sole source of atmospheric phosgene in California. Reactions which produce phosgene in the atmosphere are discussed in Section 2.5.8.1. The most important precursors of phosgene are most likely trichloroethylene, 1,1-dichloroethane, 1,1,1-trichloroethane, methylene chloride, and perchloroethylene.

25.4 INDUSTRIAL USE AND EMISSIONS

Most of the phosgene manufactured in the United States is used captively as an intermediate in the manufacture of toluene diisocyanate (55 percent), isocyanates (30 percent), and polycarbonate resins (7 percent) (Lesh and Mead, 1985). A small amount is used non-captively to produce polycarbonate resins. However, the only polycarbonate resin plants in the country are located in Indiana, Texas and West Virginia. Our discussions with phosgene producers have confirmed that it is highly unlikely that the compound is shipped to California from other states (Berry, 1985; Mamola, 1985; Panzarella, 1985; Phillips, 1985). Finally, phosgene producers are exploring ways to ship phosgene derivatives, such as diphenylcarbonate powder, which are less toxic than phosgene and less expensive to transport (Watzman and Bluestone, 1986).

Table 25.1-1

CHEMICAL DATA SUMMARY FOR PHOSGENE

Property	Value for Phosgene
CAS Registry No.	75-44-5
Synonyms	Carbonoxychloride, carbonylchloride, CG, carbonic acid dichloride, chloroformyl chloride
Molecular Weight	98.92
Molecular Formula	$COCl_2$
Molecular Structure	
Physical State at STP	Colorless gas or volatile liquid
Boiling Point	7.56°C at 760mm
Melting Point	-118°C
Specific Gravity	1.392 at 19°C/4°C
Vapor Pressure	
at 20°C	1216 mm[a]
at 25°C	1428 mm
at 30°C	1672 mm[a]
Vapor Density (air = 1)	3.42[a]
Solubility	Decomposes in H_2O
Log Partition Coefficient (octanol/H_2O)	
Henry's Law Constant	

Source: SAI (1980) unless otherwise noted.

[a] Verschueren (1977).

25.5 CONSUMER USE AND EMISSIONS

There are no consumer uses of phosgene.

25.6 EMISSION SUMMARY

Phosgene is not directly emitted to the atmosphere in California. Trichloroethylene and several other chlorinated hydrocarbons are its major precursors for atmospheric formation.

25.7 SUMMARY OF AMBIENT CONCENTRATION DATA

Ambient levels of phosgene have received very limited attention. The available information is summarized in Table 25.7-1. Urban concentrations measured in California and Phoenix, AZ are in the range 30-60 ppt and are $\leq$20 ppt at 3 sites in the Netherlands. Phosgene concentrations at more rural locations are about 15 ppt.

25.8 ATMOSPHERIC CHEMISTRY

25.8.1 In-Situ Formation

No direct emissions of phosgene into the atmosphere have been documented, and in-situ formation is believed to be the sole source of atmospheric phosgene. Phosgene is a major product of the following reactions:

- OH with chloroethenes: vinylidene chloride (Gay et al., 1976; Goodman et al., 1986), trichloroethylene (Gay et al., 1976; Goodman et al., 1986) and tetrachloroethylene (Singh et al., 1975; Lillian et al., 1975; Gay et al., 1976; Dimitriades et al., 1983; Goodman et al., 1986).

- Ozone with chloroethenes: vinylidene chloride (Hull et al., 1973), trichloroethylene (no experimental studies available) and tetrachloroethylene (Mathias et al., 1974).

Table 25.7-1

AMBIENT LEVELS OF PHOSGENE IN CALIFORNIA AND OTHER LOCATIONS

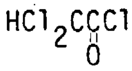
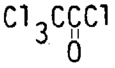
(all concentrations in ppt)

Location	Concentration		Reference
	Mean	Maximum	
Phoenix, AZ	49.7 ± 5.1	56.7	Singh et al., 1981
Los Angeles, CA	31.7 ± 8.3	61.1	Singh, 1976
Palm Springs, CA	29.3 ± 6.2	44.4	
Menlo Park, CA	30.3 ± 3.2	38.8	
Badger Pass, CA	21.6 ± 5.1	28.8	
The Netherlands (3 sites)	none detected	(≤20 ppt)	Guicherit and Schulting, 1985
Mill Valley, CA	18 (1 sample)	-	Brodzinsky and Singh, 1983
Point Arena, CA	15 (2 samples)	15	
Riverside, CA	45 (1 sample)	-	
Reese River, NV	15 (1 sample)	-	

- *Chlorine atoms with chloroethenes*: vinylidene chloride (no data available), trichloroethylene (no data available) and tetrachloroethylene (Mathias et al., 1974).

- *OH-initiated oxidation of chloromethanes*: While no data are available for this reaction, all hydrocarbons containing a CCl_2 group may yield phosgene.

- *Chlorine atoms with chloromethanes*: methylene chloride (Sanhueza and Heicklen, 1974; Spence et al., 1976) and chloroform (Sanhueza and Heicklen, 1974; Spence et al., 1976).

- *Photolysis of chloracetylchlorides*:  $HCl_2C\underset{\overset{\|}{O}}{C}Cl$ and  $Cl_3C\underset{\overset{\|}{O}}{C}Cl$ (no data available).

- *Photolysis and reaction with OH of chloroacetaldehydes*: Cl_2HCCHO and Cl_3CCHO (no data available).

Mechanisms for phosgene formation in the above reactions are outlined in Figure 25.8-1. Detailed reaction mechanisms for phosgene formation from chloroethylenes are presented in Chapter 27 (Vinylidene Chloride). Phosgene yields measured in the studies cited above are compiled in Table 25.8-1.

The relative importance of the several phosgene formation pathways can be estimated by considering the ambient concentrations of the precursors and the rates of their reactions leading to phosgene. This information is summarized in Table 25.8-2. Reaction rate constants are from the literature when available or are estimated from data for structural analogues and similar reactions. Ambient concentrations are for the Los Angeles area for all precursors for which data exist (Singh et al., 1981; Shikiya et al., 1984). Examination of the data in Table 25.8-2 indicates that concentrations of *known* precursors in Los Angeles air are more than sufficient to account for the measured ambient phosgene levels of 20-50 ppt, and that the OH-chloroethene reaction and the OH-chloromethane reactions are the major pathways for *in-situ*

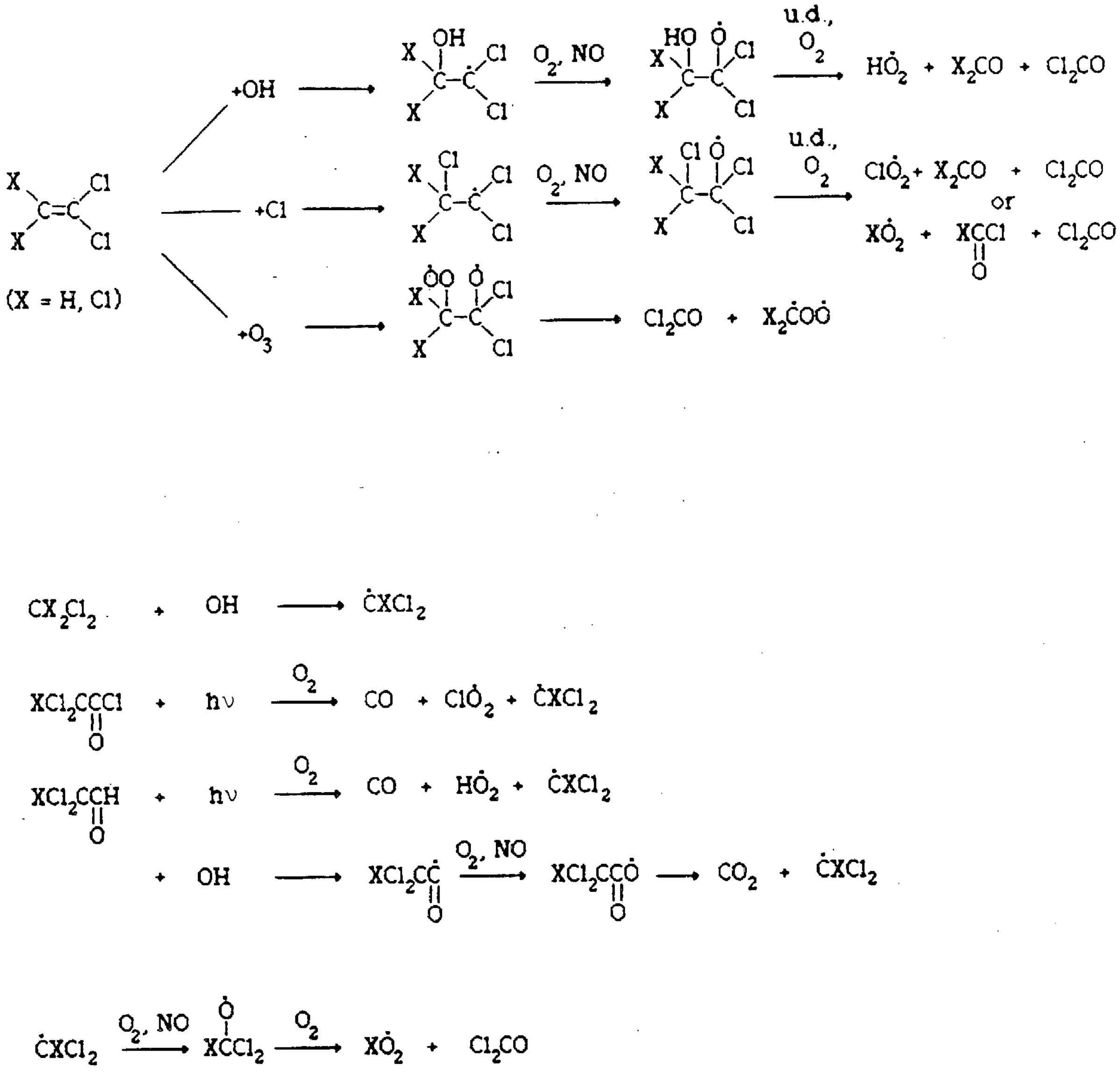


Figure 25.8-1. Phosgene Formation Mechanisms.

Table 25.8-1

PHOSGENE FORMATION YIELDS

Precursor	Reaction	Phosgene Yield[a]	Reference
Vinylidene chloride	OH	0.58	Goodman et al., 1986
		0.18	Gay et al., 1976
	O_3	0.63[a]	Hull et al., 1973
	Cl	-	
Trichloroethylene	OH	0.30	Goodman et al., 1986
		0.21	Gay et al., 1976
	O_3	-	
	Cl	-	
Tetrachloroethylene	OH	0.60	Lillian et al., 1975
		0.34	Gay et al., 1976
		0.21	Goodman et al., 1986
	O_3	large[a]	Mathias et al., 1974
	Cl	large[a]	Mathias et al., 1974
Methylene chloride	OH	-	
	Cl	0.05	Spence et al., 1976
Chloroform	OH	-	
	Cl	0.90	Spence et al., 1976
Acetylchlorides	photolysis	-	
Chloroacetaldehydes	photolysis	-	
	OH	-	

[a] Yield in molecules phosgene per molecule of precursor compound.

Table 25.8-2

PHOSGENE PRECURSORS: KINETIC DATA AND AMBIENT CONCENTRATIONS

Precursor	Ambient Levels (ppb)	Reaction	Rate Constant, cm^3 $molecule^{-1}$ sec^{-1}
Vinylidene chloride	5-10[a]	OH	6.5×10^{-12}
	<100[b]	O_3	3.7×10^{-21}
		Cl[c]	$<6 \times 10^{-11}$
Trichloroethylene	400-1,700[a]	OH	2.4×10^{-12}
	500-1,000[b]	O_3	$<3 \times 10^{-20}$
		Cl[c]	$\leq 2 \times 10^{-11}$
Tetrachloroethylene	1,500-2,000[a]	OH	0.17×10^{-12}
	1,400-2,800[b]	O_3	$<2 \times 10^{-23}$
		Cl[c]	$\leq 7 \times 10^{-12}$
Methylene chloride	3,700-12,000[a]	OH	1.4×10^{-13}
	600-2,500[b]	Cl	5.2×10^{-13}
Chloroform	80-200[a]	OH	1.0×10^{-13}
	10-150[b]	Cl	1.23×10^{-13}
Chloroacetyl chlorides	No data	Photolysis	Slow?[d]
Chloroacetaldehydes	No data	Photolysis	Fast (∿same as acetaldehyde)
		OH[e]	$\sim 10^{-11}$

---

[a] Singh et al., 1981.

[b] Shikiya et al., 1984.

[c] Estimated to be ≤10 times faster than the OH reaction.

[d] Dimitriades et al. (1983) report a photolysis rate of 6 percent per hour for trichloroacetyl chloride.

[e] Estimated to be same as for OH + acetaldehyde.

formation of phosgene in the atmosphere. Reactions with ozone are essentially negligible. Reactions with chlorine atoms are fast but concentrations of chlorine in urban air are presumably too low for this reaction to be important. Chloroacetyl chlorides and chloroacetaldehydes, for which no kinetic and ambient level data are available, cannot be assessed at the present time.

Finally, we attempted to rank the possible precursors of phosgene by using the product of their ambient (Los Angeles) concentrations and their OH reaction rate constant. This information is summarized in Table 25.8-3, where all products of concentrations and rate constants are listed relative to that of vinylidene chloride. Table 25.8-3 indicates that the five major precursors of phosgene in Los Angeles air are, in order of decreasing importance: trichloroethylene, 1,1-dichloroethane, 1,1,1-trichloroethane, methylene chloride, and tetrachloroethylene.

25.8.2 Removal Processes

Once formed, phosgene is removed only slowly from the atmosphere. Its reactions with OH, O_3, NO_3 and Cl are of negligible importance. Photolysis and gas phase hydrolysis are also deemed negligible on the basis of laboratory studies in which phosgene was stable for $\geq$ 15 hours in air containing about 10,000 ppm of water vapor under irradiation conditions approximating those of sunlight (Singh, 1976). Phosgene is therefore removed from the troposphere only by deposition and upward diffusion.

25.9 REFERENCES

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Table 25.8-3
RELATIVE IMPORTANCE OF PHOSGENE PRECURSORS

Precursor	A = OH Reaction Rate Constant $10^{-12}\,cm^3\,molecule^{-1}\,sec^{-1}$	B = Ambient Concentration (ppt)	Product A x B	Ranking
Vinylidene chloride	6.5	5 - 10	32 - 65	4
Trichloroethylene	2.4	500 - 1,000	500 - 2400	1
Tetrachloroethylene	0.17	1,400 - 2,800	238 - 476	3
Methylene chloride	0.14	600 - 5,000	84 - 700	2
Chloroform	0.10	50 - 200	5 - 20	6
Carbon tetrachloride	<0.001	215	<0.21	-
Hexachloro-1,3-butadiene	0.17	4	0.7	10
1,1-dichloroethane	0.26	66	17	5
1,1,1-trichloroethane	0.01	1,030	10.3	7
1,1,2-trichloroethane	0.33	9	2.9	8
1,1,1,2-tetrachloroethane	<0.01	4	<0.04	-
1,1,2,2-tetrachloroethane	<0.01	12	<0.12	-
Hexachloroethane	<0.001	ND[a]	(small)	-
Bromodichloromethane	0.1	10	1.0	9
Fluorotrichloromethane	<0.001	470	<0.47	-
CF_3CCl_3	<0.001	300	<0.30	-

[a] ND = no data.

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26.0

EVALUATION OF PROPYLENE OXIDE

26.1 PHYSICAL AND CHEMICAL PROPERTIES

Propylene oxide (PO) is a colorless, highly flammable liquid. Table 26.1-1 summarizes some of its physical and chemical properties.

26.2 DIRECT PRODUCTION IN CALIFORNIA

None of the six producers of propylene oxide is located in California (McCurdy, 1985).

26.3 INDIRECT PRODUCTION AND EMISSIONS IN CALIFORNIA

Propylene oxide is not produced through any combustion processes. No indirect production of PO in the state is believed to occur.

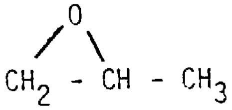
26.4 INDUSTRIAL USE AND EMISSIONS

According to the Chemical Economics Handbook (SRI, 1982), about 64 percent of the propylene oxide available in the U.S. is used as a chemical intermediate for the production of urethane polyols. It is also used to manufacture propylene glycol (19 percent), dipropylene glycol (2 percent), and glycol ethers (2 percent). Propylene oxide is also used as a fumigant in packaged food products and as a solvent in coatings. Nationwide production and use, which was declining in the early 1980s (Anon., 1980, 1984), is expected to increase by more than 4 percent per year betwen 1983 and 1989, due to growth in construction and transportation markets (Lesh and Mead, 1985).

According to the "best estimate" of one major propylene oxide manufacturer, California firms use up to 5 million lb/yr of propylene oxide (Bergeson, 1986). Industrial uses in California, as identified by the South Coast Air Quality Management District toxic pollutant emission inventory survey (Zwiacher et al., 1983) and our own research, include:

Table 26.1-1

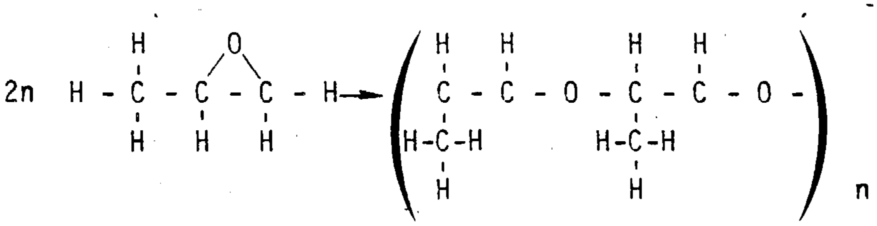
CHEMICAL DATA SUMMARY FOR PROPYLENE OXIDE

Property	Value for Propylene Oxide
CAS Registry No.	75-56-9
Synonyms	Propene oxide, methyl oxirane, 1,2 epoxy propane, epoxypropane, methyl ethylene oxide, propene oxide, propyleneoxide, 1,2-propylene oxide
Molecular Weight	58.08
Molecular Formula	C_3H_6O
Molecular Structure	 $\overset{O}{CH_2 - CH} - CH_3$
Physical State at STP	Colorless liquid
Boiling Point	33.9°C at 760 mm
Melting Point	-104.4°C
Specific Gravity	0.8394 at 20°C/4°C
Vapor Pressure	596 mm at 25°C
Vapor Density (air=1)	2.00
Solubility	Soluble (650 gm/L of H_2O at 30°C)
Log Partition Coefficient (octanol/H_2O)	
Henry's Law Constant	

Source: SAI (1980).

- Intermediate in polyurethane polyols
- Intermediate in polyethylene glycol-fatty acid esters
- Stabilizer in coatings
- Process solvent
- Propoxylating agent in food additive production

A "polyol" is an organic alcohol containing three or more hydroxyl groups; polyether polyols are produced by the addition of PO to polyols, such as glycerin or propylene glycol, in an alkaline solution at elevated temperatures and pressures above 4 atmospheres (Lesh and Mead, 1985). Polyols can also be produced by the following reaction (Coco et al., 1979):



$$2n\ \mathrm{H-\overset{H}{\underset{H}{C}}-\overbrace{\underset{H}{C}-\underset{H}{C}}^{O}-H} \longrightarrow \left(\mathrm{\overset{H}{\underset{\underset{H}{H-C-H}}{C}}-\overset{H}{C}-O-\overset{H}{\underset{\underset{H}{H-C-H}}{C}}-\overset{H}{C}-O-} \right)_n$$

Urethane polyols are used primarily as foams for the automotive and furniture industries. The main sources of emissions from polyol production are process ventings, storage and fugitive releases.

Table 26.4-1 summarizes facility-specific PO emission estimates prepared by the South Coast Air Quality Management District (SCAQMD), the Bay Area Air Quality Management District (BAAQMD), and the U.S. Environmental Protection Agency. The SCAQMD estimated emissions of 3.5 tons (3.2 kkg) per year, while the BAAQMD estimated that emissions from the facilities in its survey were between 0 and 0.1 tons per year; thus the total for the BAAQMD would be 0 - 1.1 tons/yr. According to the San Diego Air Pollution control District (Lake, 1986), propylene oxide emissions from a plant operated by Kelco in San Diego were 175 and 158 tons in 1983 and 1984, respectively. Statewide emissions are therefore estimated to be 162 - 163 tons/yr (147 - 148 MT/yr).

Examination of the original questionnaires and the emission calculations by the SCAQMD revealed a wide variety of estimation methods. In many cases, the SCAQMD assumed a loss rate of 1 percent in manufacturing. In

Table 26.4-1

REPORTED PROPYLENE OXIDE EMITTERS IN CALIFORNIA

Firm	City	County	Emission Estimate SCAQMD lb/yr	Emission Estimate SCAQMD kg/yr	Emission Estimate BAAQMD lb/yr	Emission Estimate BAAQMD kg/yr
American Can Company	Carson	Los Angeles	20	9.1		
Ampex Corporation		San Mateo			T[a]	T
Amvac Chemical Corp.	Los Angeles	Los Angeles	2,000	907.0		
Bauer Coating & Chemical	Los Angeles	Los Angeles	1	.5		
Bee Chemical Company	Gardena	Los Angeles	11	5.0		
Benjamin Moore & Company	Commerce	Los Angeles	1	.5		
Brunswick Corp, Defense Division	Costa Mesa	Orange	14	6.3		
Continental Can Co. Plant #11	Los Angeles	Los Angeles	174	78.9		
Dow Chemical Company	Pittsburg	Contra Costa			U[a]	U
Fuller-O'Brien Div.	S. San Francisco	San Mateo			T	T
Gatx	San Pedro	Los Angeles	1	.5		
Glidden Coatings & Resin	San Francisco	San Francisco			T	T
Great Western Chemical Company	Richmond	Contra Costa			T	T
Inland Specialty Chemical Corp.	Costa Mesa	Orange	15	6.8		
IT Corporation, Oil Reprocessing	Martinez	Contra Costa			U	U
Koppers Company Inc.	Vernon	Los Angeles	1	.5		
Lawrence Livermore National Lab.	Livermore	Alameda			T	T
Lilly Industrial Coatings Inc.	Montebello	Los Angeles	6	2.7		
Lonza Inc.	Long Beach	Los Angeles	1,160	526.1		
Magna Corporation	Santa Fe Springs	Los Angeles	15	6.8		
Midland Division	Hayward	Alameda			T	T
Mobile Chemical Company	Azusa	Los Angeles	30	13.6		
Neville Chemical Company	Santa Fe Springs	Los Angeles	40	18.1		
Pervo Paint Company Inc.	Los Angeles	Los Angeles	156	70.7		
Pierce & Stevens Chemical	Milpitas	Santa Clara			T	T
PTM&W Ind. Inc.	Santa Fe Springs	Los Angeles	7	3.2		
Reliance Universal Inc.	Brea	Orange	7	3.2		
Sherwin-Williams Company	Emeryville	Alameda			T	T
Specialty Finishers Company	Rancho Cucamonga	Riverside	4	1.8		
Tnemec Company of CA, Inc.	Compton	Los Angeles	3	1.4		
Tretolite, Div. Petrolite Corp.	Brea	Orange	3,344	1,516.6		
Union Oil of CA S/T Div.	Brea	Orange	7	3.2		
United Can Company	Hayward	Alameda			T	T
Totals			7,017	3,182.3	0	0

Source: Summarized from emissions reported by the South Coast Air Quality Management District (Zwiacher et al., 1983) and the Bay Area Air Quality Management District (Hill, 1985).

[a] T = Emissions are 0-0.1 ton/yr; U = Propylene oxide is used but emissions are unknown.

one case, the manufacturer's estimate of 2 percent was accepted. In yet another case, 0.1 percent was used. These may be compared with an emission factor of 0.000132 lb per lb PO used, which is based on information reported by Texas chemical plants to the Texas Air Control Board (SAI, 1980). The Texas emission factor was used in compiling the EPA Region IX emission inventory (Lesh and Mead, 1985). Therefore the SCAQMD emission estimate may be high by at least one order of magnitude. This is an area whose uncertainty may need to be reduced in Phase II.

Finally, the extent to which propylene oxide is used as a fumigant in the state is unknown. It is not considered a "restricted material" by the Department of Food and Agriculture," and is therefore not included in Pesticide Use Reports (Gatenby, 1986).

26.5 CONSUMER USE AND EMISSIONS

As noted in Section 26.4, propylene oxide is used as a stabilizer in coatings, and thus may be present in several consumer products. In consideration of its function, it is reasonable to assume that propylene oxide would undergo chemical reactions rather than be emitted from the coatings. Nevertheless, emissions from consumer use constitutes another area of uncertainty. Finally, emissions of residual propylene oxide in processed food could also occur.

26.6 EMISSION SUMMARY

California emissions of propylene oxide are estimated to be about 160 tons per year, largely from one source in San Diego County. Some additional emissions may occur through consumer use of paints and coatings containing PO as a stabilizer and evaporation of residual PO used in food processing. All of the emission estimates presented here are highly uncertain.

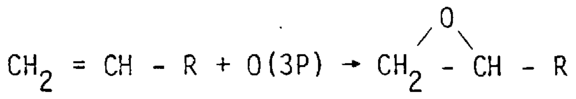
26.7 SUMMARY OF AMBIENT CONCENTRATION DATA

No ambient concentration data are available for propylene oxide.

26.8 ATMOSPHERIC CHEMISTRY

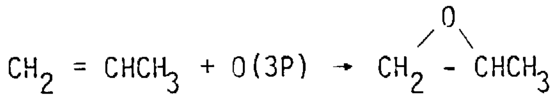
26.8.1 In-Situ Formation

The reaction of atomic oxygen with olefins lead to epoxides:



$$CH_2 = CH - R + O(3P) \rightarrow \overset{O}{CH_2 - CH} - R$$

Accordingly, propylene oxide may form by reaction of O(3P) with propene:



$$CH_2 = CHCH_3 + O(3P) \rightarrow \overset{O}{CH_2 - CHCH_3}$$

However, this reaction is not expected to be important in the atmosphere. Propene also reacts rapidly with ozone, with the hydroxyl radical, and with the nitrate radical to form products other than propylene oxide. Concentrations of oxygen atoms in the lower troposphere are too low, relative to those of OH, O_3 and NO_3, for the propene-O(3P) reaction to compete with the reactions of propene with OH, O_3 and NO_3.

26.8.2 Removal Processes

Photolysis of propylene oxide and its reactions with O_3 and NO_3 are negligible. Daytime removal by reaction with OH is expected, though at a slow rate. The OH-propylene oxide reaction rate constant has been measured, $k_{OH} = 1.3 \times 10^{-12}$ cm^3 $molecule^{-1}$ sec^{-1}. No product studies have been carried out, and a tentative reaction mechanism is proposed in Figure 26.8-1. H-atom abstraction is expected to involve the tertiary C_2 hydrogen atom, and, to a lesser extent, the secondary C_1 hydrogen atoms. Both pathways are included in Figure 26.8-1. For each alkoxy radical, unimolecular decomposition may involve C-C as well as C-O bond scission, leading to formaldehyde, $CH_3\dot{C}O$, acetaldehyde, and HCO (which reacts with O_2 to give carbon monoxide and $HO_2^{\bullet}$). Acetaldehyde (by reaction with OH) and CH_3CO will lead to peroxyacetyl nitrate (PAN).

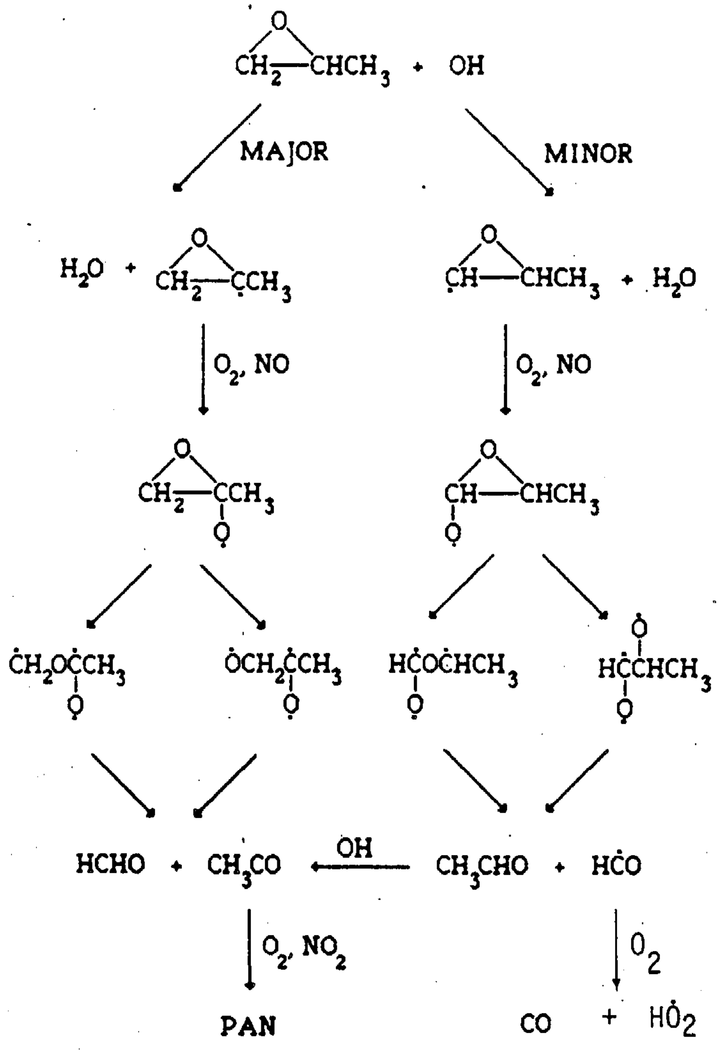


Figure 26.8-1. OH-Propylene Oxide Reaction.

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27.0

EVALUATION OF VINYLIDENE CHLORIDE

27.1 PHYSICAL AND CHEMICAL PROPERTIES

Vinylidene chloride (VDC) is a highly reactive, flammable, clear colorless liquid. Table 27.1-1 summarizes some of its physical and chemical properties.

27.2 DIRECT PRODUCTION IN CALIFORNIA

Vinylidene chloride is produced by two companies at three facilities in Texas and Louisiana (Hushon and Korneich, 1978). There is no California production.

27.3 INDIRECT PRODUCTION AND EMISSIONS IN CALIFORNIA

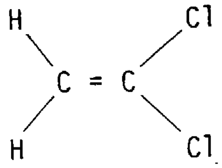
A recent evaluation of data from municipal wastewater treatment plants (Chang et al., 1987) found that wastewater treatment processes in California release about 2.75 tons per year of vinylidene chloride. About 85 percent of these emissions (2.33 tons per year) occur at three plants: The Hayward Wastewater Treatment Facility (Hayward), The South Bayside WWTF (Redwood City), and The Los Angeles Hyperion Treatment Plant.

27.4 INDUSTRIAL USES AND EMISSIONS

The chief industrial use of VDC is as a comonomer with vinyl chloride, alkyl acrylate or acrylonitrile in saran (Hushon and Kornreich, 1978). A recent inventory of toxic air pollutant sources, prepared for the U.S. Environmental Protection Agency's Region IX (Bloomhardt and Pelland, 1985), listed three facilities in California (Oscar Mayer Company in Los Angeles, Cryovac in Camarillo, and Borden Chemical Division in Compton) in which VDC copolymer is used to make packaging material. Two of the facilities

Table 27.1-1

CHEMICAL DATA SUMMARY FOR VINYLIDENE CHLORIDE

Property	Value for Vinylidene Chloride
CAS Registry No.	
Synonyms	1,1-dichlorethylene, VDC, sconatex, 1,1-DEC, vinylidene dichloride
Molecular Weight	96.95
Molecular Formula	$C_2H_2Cl_2$
Molecular Structure	
Physical State at STP	Colorless liquid
Boiling Point	31.56°C at 760 mmHg/14.43°C at 400 mm Hg
Melting Point	-122.5°C
Specific Gravity	
Vapor Pressure[a]	500 mm at 20°C
Vapor Density (air=1)	3.34
Solubility	In water at 25°C wt %: 0.021
Log Partition Coefficient (octanol/H_2O)[b]	1.84
Henry's Law Constant	34.0 atm-L/mole

Source: SAI (1980) unless otherwise noted.

[a] Verschueren (1977).

[b] ICF (1985).

are also cited in another EPA compilation (USEPA, 1985). According to the EPA's Pollutant Assessment Branch, these compilations are based upon data collected in the late 1960s and early 1970s (Pate, 1986). Calls to Oscar Mayer and Borden confirmed that the compound is either no longer used or never was used at these facilities. Because we were unable to locate the plant in Camarillo, we contacted the Ventura County Air Pollution Control District (Katayama, 1986), which stated that it had no records of the facility in question.

Table 27.4-1 summarizes the results of a Bay Area Air Quality Management District survey of toxic air pollutant emissions in its jurisdiction (Hill, 1985). The only source greater than 0.1 ton/year is Guardian Packaging Corporation in Newark, which uses VDC to manufacture saran for coating polystyrene container lids (Stanley, 1986). Three other facilities emit between 0 and 0.1 tons per year, so total emissions in the area are 1.1 - 1.4 tons/yr (1.0 - 1.3 MT/yr).

VDC is also used as a chemical intermediate in methyl chloroform (1,1,1-trichloroethane) production. However, a previous investigation confirmed that no methyl chloroform is produced in California (Rogozen et al., 1985). Finally vinylidene chloride is a comonomer for modacrylic fibers and barrier coatings on paper products and plastic films. Information on modacrylic fiber production in California is unavailable.

27.5 CONSUMER USE AND EMISSIONS

There are no direct consumer uses of vinylidene chloride. It is possible that some VDC may volatilize from saran and other films for which it is a copolymer, but no information on these potential emissions is available.

Table 27.4-1

VINYLIDENE CHLORIDE EMISSIONS IN THE SAN FRANCISCO BAY AREA

Source	City	Emissions (tons/yr)
Alameda County		
Clorox Technical Center	Pleasanton	U
Drew Refining Company	Berkeley	T
Guardian Packaging Corp.	Newark	1.1
Lawrence Livermore National Laboratory	Livermore	U
Packaging Industries, Inc.	San Leandro	U
Contra Costa County		
Dow Chemical Company	Pittsburg	U
San Mateo County		
Deluxe Packages	S. San Francisco	T

Source: Bay Area Air Quality Management District (Hill, 1985).

[a] T = 0-0.1 tons/yr; U = Vinylidene chloride is handled but emissions cannot be estimated from available information.

27.6 EMISSION SUMMARY

The only likely sources of vinylidene chloride emissions in California are manufacture of VDC copolymers and releases from wastewater treatment processes. Emissions from these sources in the San Francisco Bay area are about 3.2 - 3.5 tons/yr (2.9 - 3.2 MT/yr). Emissions in the rest of the state are about 0.6 ton/yr (0.5 MT/yr), for a total of 3.8 - 4.1 tons/yr (3.4 - 3.8 MT/yr).

27.7 SUMMARY OF AMBIENT CONCENTRATION DATA

Several studies of toxic air contaminants have included measurements of ambient levels of vinylidene chloride (Table 27.7-1). Singh et al. (1981) reported mean values of about 5, 13, and 30 ppt in Los Angeles and Oakland, CA, and Phoenix, AZ. The corresponding maxima were about 10, 25 and 37 ppt. Brodzinsky and Singh (1983) have compiled data for 30 locations in the U.S., including Riverside, CA (mean = 6.5 ppt, maximum = 14.0 ppt). Guicherit and Schulting (1985) measured CH_2CCl_2 at three sites in the Netherlands. All three data sets are consistent and indicate typical values of 5-30 ppt, with maxima of 10-140 ppt. Measurements taken in industrial areas near sources of CH_2CCl_2 obviously yielded much higher values, 38×10^3 ppt (mean) and 67×10^3 ppt (maxima).

An ongoing Air Resources Board monitoring study of toxic air contaminants at four sites in the Los Angeles area includes 24-hour measurements of vinylidene chloride. The initial results, covering November 1982 to December 1983, have been reported by Shikiya et al. (1984). More recent results, for January - August 1984, have been made available to us by the ARB (McNerny, 1985). The stated detection limit for CH_2CCl_2 is 100 ppt, and no vinylidene chloride has been detected in the 541 samples for which the ARB provided us with results. Examination of the data in Table 27.7-1 indicates that urban levels of CH_2CCl_2 measured by other investigators are well below the detection limit of the ARB monitoring study.

Table 27.7-1

AMBIENT LEVELS OF VINYLIDENE CHLORIDE

(Concentrations in ppt)

Location	Vinylidene Chloride Mean	Vinylidene Chloride Maximum	Reference
Los Angeles, CA	4.9	9.7	Singh et al., 1981
Oakland, CA	12.6	24.4	
Phoenix, AZ	29.8	36.8	
Delft, Vlaardingen and Terschelling, The Netherlands	5-12	10-25	Guicherit and Schulting, 1985
Riverside, CA	6.5	14.0	Brodzinski and Singh, 1983
33 U.S. locations outside of California:			
urban-surburban:	8.0	140	
near source	38×10^3	67×10^3	
Los Angeles, CA	ND[c]	ND	Shikiya et al., 1984[a] and Air Resources Board[b]
El Monte, CA	ND	ND	
Dominguez Hills, CA	ND	ND	
Riverside, CA	ND	ND	

[a] November 1982 - December 1983.

[b] January - August 1984 (McNerny, 1985).

[c] ND = none detected (<100 ppt).

27.8 ATMOSPHERIC CHEMISTRY

27.8.1 In-Situ Formation

There are no known reactions that would lead to the in-situ production of vinylidene chloride in the atmosphere. Reaction of chlorine atoms with olefins does not involve substitution pathways and proceeds by addition on the unsaturated C=C bond. For example, the reactions of ethylene with chlorine atoms does not lead to 1,1-dichloroethene (vinylidene chloride) but yields formaldehyde and formyl chloride:

$$CH_2 = CH_2 + Cl \rightarrow CH_2Cl\text{-}\dot{C}H_2$$

$$CH_2Cl\dot{C}H_2 + O_2,\ NO \rightarrow CH_2Cl\ C(\dot{O})H_2$$

$$CH_2ClC(\dot{O})H_2 \rightarrow \underline{HCHO} + H_2\dot{C}Cl$$

$$H_2\dot{C}Cl + O_2, NO \rightarrow H_2C(\dot{O})Cl$$

$$H_2C(\dot{O})Cl + O_2 \rightarrow H\underset{\underset{O}{\|}}{C}Cl + H\dot{O}_2 \text{ and/or } \underline{HCHO} + Cl\dot{O}_2$$

Formyl chloride, HCOCl, is thermally unstable and decomposes to CO + HCl.

27.8.2 Removal Processes

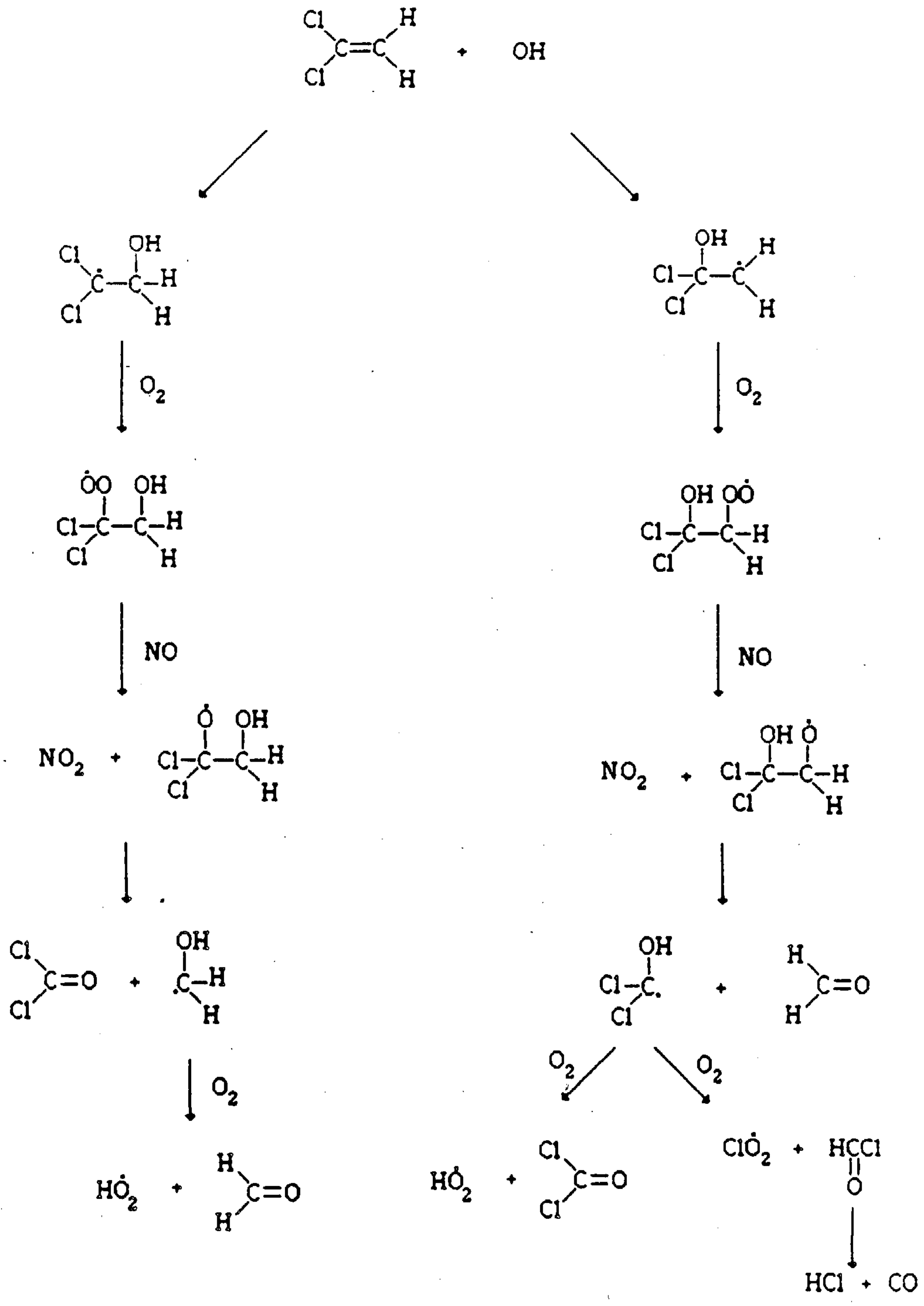
Photolysis, reaction with ozone ($k = 3.7 \times 10^{-21}$ cm^3 molecule^{-1} sec^{-1}) and reaction with NO_3 ($k \sim 5.5 \times 10^{-15}$ cm^3 molecule^{-1} sec^{-1}, estimated from structure-reactivity relationships) are of negligible importance for atmospheric removal of vinylidene chloride. The atmospheric persistence of CH_2CCl_2 is controlled by its reaction with the hydroxyl radical. The rate constant we estimated from structure-reactivity relationships is $K_{OH} \sim 2.6 \times 10^{-11}$ cm^3 molecule^{-1} sec^{-1}. The only, and very recent (Goodman et al., 1986) experimental value is about one fourth the estimated value, or 6.5×10^{-12} cm^3 molecule^{-1} sec^{-1}. With this rate constant and an estimated OH concentration of 5×10^5 radicals cm^{-3} (24-hour average), the atmospheric lifetime of vinylidene chloride is about 4 days.

The exact mechanism of the OH-vinylidene chloride reaction is not known. One major component of this mechanism involves the "normal" pathway of OH addition to olefins, as is shown in Figure 27.8-1. This pathway includes the steps of OH addition to the C=C bond, reaction of the two hydroxyalkyl radicals with O_2 to give peroxy radicals, peroxy radical reaction with NO to give alkoxy radicals, and unimolecular decomposition into phosgene ($Cl_2C=O$) and formaldehyde ($H_2C=O$). The $Cl_2\dot{C}OH$ radical is expected to react with O_2 by H-atom abstraction to form phosgene and $H\dot{O}_2$. An alternate pathway may involve Cl-atom abstraction from the weak C-Cl bond to form ClO_2 and formyl chloride, which thermally decomposes into CO and HCl.

Only two studies of the reaction products have been carried out. Goodman et al. (1986) identified phosgene as a major product (yield = 58 percent): no other products were identified. Gay et al. (1976) reported phosgene (18 percent), CO (22 percent) HCl (28 percent), formaldehyde (yield not reported), formic acid (yield not reported) and chloroacetyl chloride, $ClH_2C\underset{\underset{O}{\|}}{C}Cl$ (yield not reported, listed as "major" product). The first four products are consistent with the OH reaction mechanism shown in Figure 27.8-1. Formic acid is a product of the ozone-vinylidene chloride reaction (Figure 27.8-2); large amounts of ozone were formed in the NO_2-CH_2CCl_2 irradiation experiments of Gay et al. (1976).

The observation of chloroacetyl chloride, however, cannot be rationalized in terms of the OH reaction mechanism shown in Figure 27.8-1. Other reaction pathways that yield chloroacetyl chloride may include:

- The reactions of ozone with CH_2CCl_2: Hull et al. (1973) observed chloroacetyl chloride as a product resulting from a chain reaction involving recombination of a Criegee biradical with CH_2CCl_2. This reaction may account for chloroacetyl chloride formation in the experiment of Gay et al. (1976), in which large amounts of ozone were produced from 5 ppm CH_2CCl_2 and 2 ppm NO_2. However, such radical-molecule reaction will be negligible at much lower levels of CH_2CCl_2 in the atmosphere (5-20 ppt, see Table 27.7-1).



NET: $Cl_2C{=}O$ + $H_2C{=}O$ + $H\dot{O}_2$ NET: H_2CO + ($Cl_2C{=}O$ and/or HCl + CO)

Figure 27.8-1. OH-Vinylidene Chloride Reaction: OH-Olefin Addition Pathway.

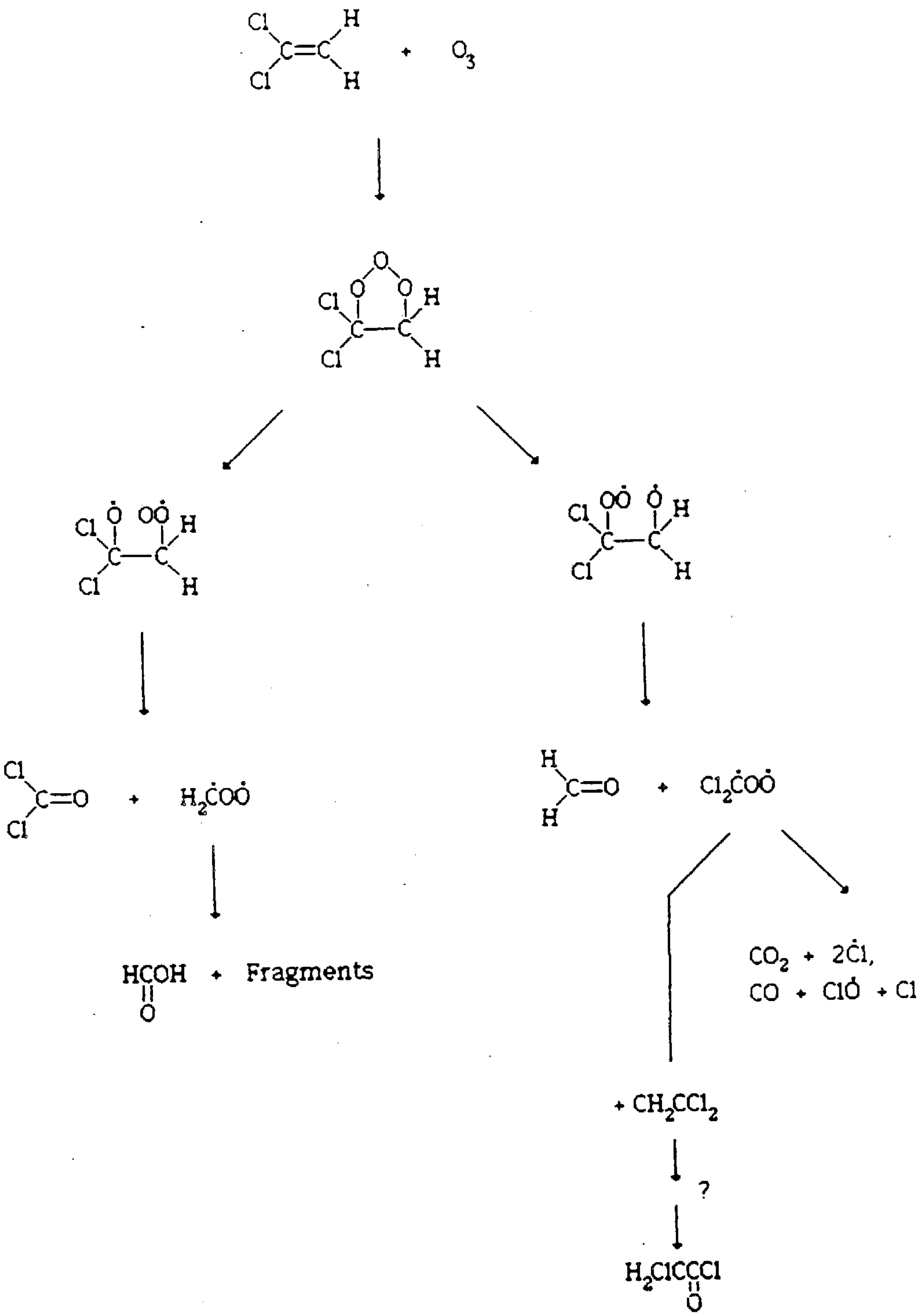
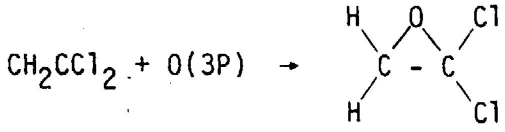
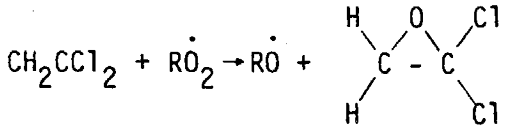
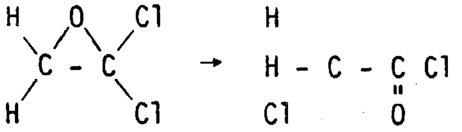


Figure 27.8-2. Ozone-Vinylidene Chloride Reaction.

- Formation of an epoxide by reaction of CH_2CCl_2 with oxygen atoms or with peroxy radicals, and rearrangement to chloroacetyl chloride by 1,2-chlorine atom transfer (Gay et al., 1976):







The proposed epoxide rearrangement is reasonable, but its formation by reactions of CH_2CCl_2 with oxygen atoms or peroxy radicals is expected to be negligible at low concentrations in the atmosphere.

- Reaction of vinylidene chloride with chlorine atoms, as suggested by Howard (1976) for tetrachloroethylene. As is shown in Figure 27.8-3, chloroacetaldehyde is indeed expected to form from Cl + CH_2CCl_2 by simple reaction steps analogous to those involved in the OH + CH_2CCl_2 reaction. Unlike the two reactions discussed above, this third pathway could yield chloroacetaldehyde under atmospheric conditions, provided that chlorine atoms are present in sufficient amounts. Chlorine atoms may form in the chloroethene-OH reaction as suggested by Howard (1976) for tetrachloroethylene (Figure 27.8-4). This will not, however, produce enough chlorine atoms at low (ppt) levels of CH_2CCl_2 in urban air.

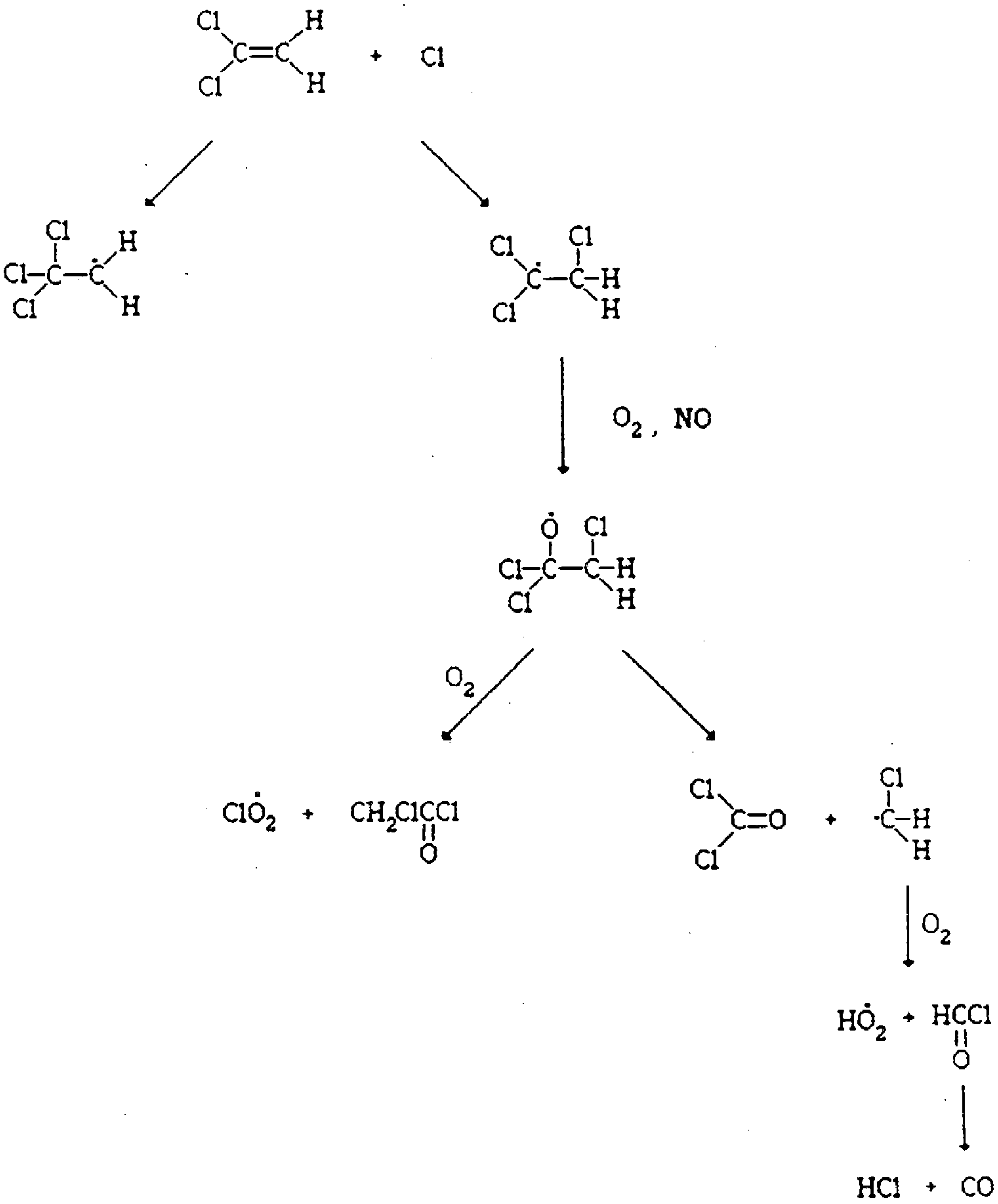


Figure 27.8-3. Formation of Chloroacetyl Chloride in the Chlorine - Vinylidene Chloride Reaction.

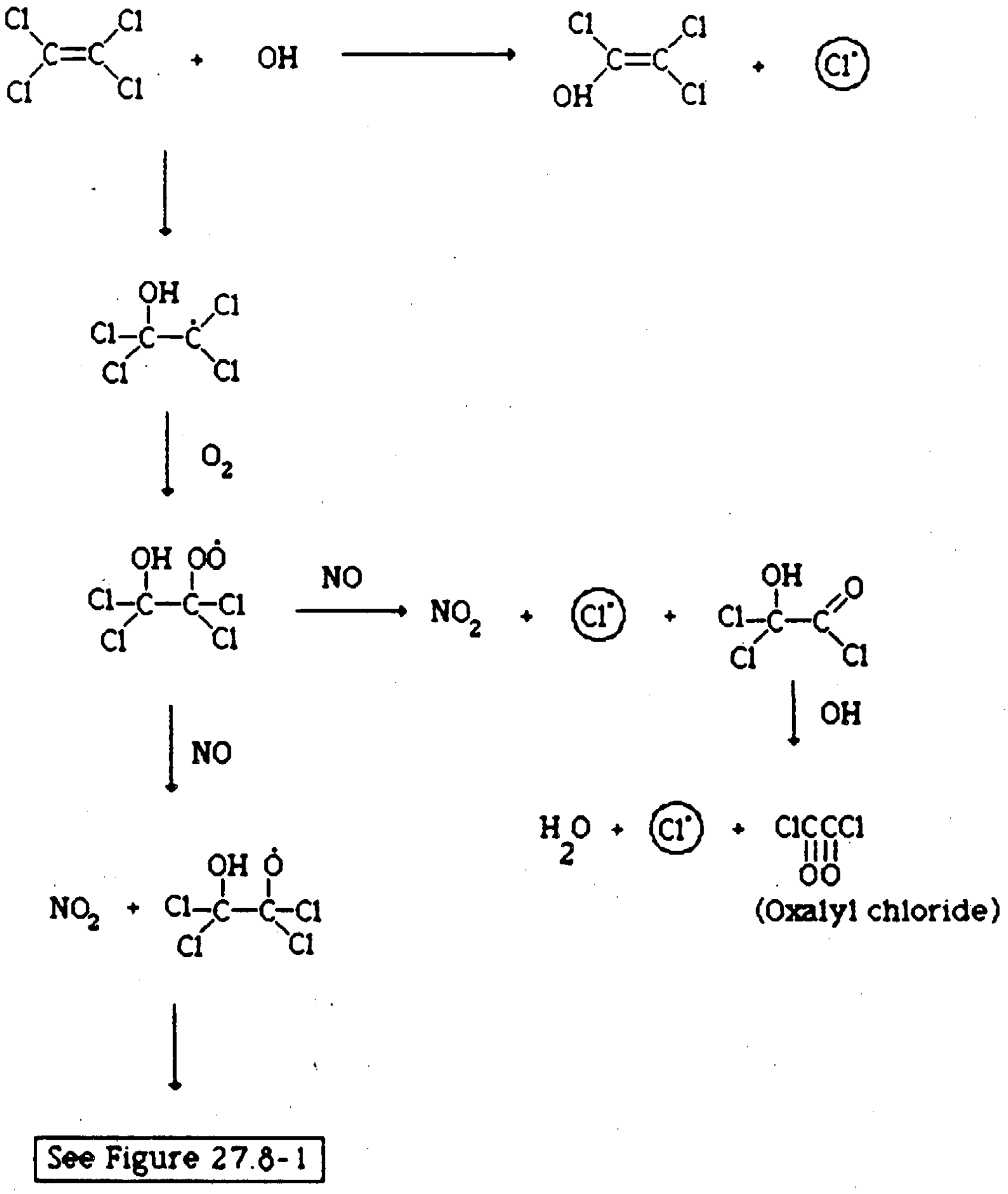


Figure 27.8-4. Formation of Chlorine Atoms in the OH-Tetrachloroethylene Reaction (Adapted from Howard, 1976). Subsequent Reactions of Cl With $Cl_2C=CCl_2$ Lead to Trichloroacetyl Chloride ($Cl_3C\underset{O}{C}Cl$) and Chlorine Atoms. The "Normal" OH-Olefin Reaction Sequence is Shown on the Left; See Figure 27.8-1.

To summarize, the OH-vinylidene chloride reaction is expected to yield formaldehyde and phosgene as major products according to the "normal" OH-olefin reaction mechanism shown in Figure 27.8-1. Formation of chloroacetyl chloride, as observed by Gay et al. (1976), may involve three pathways. Of these, two are negligible under atmospheric conditions (ppt levels of CH_2CCl_2), and the third may occur provided that an "external supply" of chlorine atoms be available. Urban levels of chlorine are undocumented. They are presumably too low for the $Cl + CH_2CCl_2 \rightarrow ClH_2C\underset{\underset{O}{\|}}{C}Cl$ reaction to be important in urban air.

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28.0

EVALUATION OF XYLENE(S)

28.1 PHYSICAL AND CHEMICAL PROPERTIES

The xylenes are colorless liquids at standard temperature and pressure. Tables 28.1-1 through 28.1-3 summarize some of their physical and chemical properties.

28.2 DIRECT PRODUCTION IN CALIFORNIA

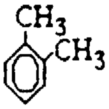
Most commercialy produced xylene isomers occur as mixed xylenes in an aromatic mixture (BTX) along with benzene and toluene. By far the greatest portion of mixed xylenes are produced in the U.S. by catalytic reforming of petroleum during the cracking of hydrocarbons. The aromatic fractions are isolated from the reformate by extraction and distillation. This process produces ten times the amount of mixed xylenes as pyrolysis gasoline, the next largest manufacturing process. A third process for the manufacture of mixed xylenes is the disproportionation of toluene. The final method involves production from coal-derived BTX (SAI, 1980).

In 1978, 201 facilities produced mixed xylenes from catalytic reformate. Of these, 29 plants isolated mixed xylenes from the reformate. Only one plant, operated by Chevron Chemicals in Richmond, was located in California. This manufacturing facility ceased operations several years ago (Williams, 1986). We are not certain whether any of the remaining facilities, which produce non-isolated xylenes, are presently located in California. None of the nine producers of mixed xylenes from pyrolysis gasoline, or the two companies that produce coal-derived mixed xylenes at three sites, or the two that produce mixed xylenes from toluene disproportionation, is located in the state (SAI, 1980).

The majority of nonisolated mixed xylenes as BTX are blended into gasoline. Isolated mixed xylenes are used in a variety of solvent applications and to produce individual xylene isomers. Almost 50 percent of isolated mixed xylene production was used in the manufacture of p-xylene,

Table 28.1-1

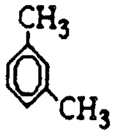
CHEMICAL DATA SUMMARY FOR O-XYLENE

Property	Value for o-xylene
CAS Registry No.	95-47-6
Synonyms	o-xylol, dimethylbenzene
Molecular Weight	106.2
Molecular Formula	C_8H_{10}
Molecular Structure	
Physical State at STP	Colorless liquid
Boiling Point	144.4°C at 760mm
Melting Point	-25°C
Specific Gravity	0.8880 at 20°C/4°C
Vapor Pressure	10 mm at 32.1°C
Vapor Density (air = 1)	3.67[a]
Solubility	Insoluble (H_2O)
Log Partition Coefficient (octanol/H_2O)	2.77
Henry's Law Constant	

Source: SAI (1980).

[a] Calculated assuming molecular weight of air to be 28.962.

Table 28.1-2
CHEMICAL DATA SUMMARY FOR M-XYLENE

Property	Value for m-xylene
CAS Registry No.	108-38-3
Synonyms	1,3-dimethylbenzene
Molecular Weight	106.16
Molecular Formula	$CH_3C_6H_4CH_3$
Molecular Structure	
Physical State at STP	colorless liquid
Boiling Point	139°C
Melting Point	-48/-53°C
Specific Gravity	
Vapor Pressure	6 mm @ 20°C, 11 mm @ 30°C
Vapor Density (air=1)	3.66
Solubility	
Log Partition Coefficient (octanol/H_2O)	
Henry's Law Constant	

Source: SAI (1980).

Table 28.1-3

CHEMICAL DATA SUMMARY FOR P-XYLENE

Property	Value for p-xylene
CAS Registry No.	106-42-3
Synonyms	p-dimethylbenzene; 1,4-dimethylbenzene
Molecular Weight	106.17
Molecular Formula	$(CH_3)_2C_6H_4$
Molecular Structure	
Physical State at STP	Colorless
Boiling Point	138.4°C
Melting Point	13°C
Specific Gravity	
Vapor Pressure	6.5 mm @ 20°C, 12 mm @ 30°C
Vapor Density (air=1)	3.7
Solubility	0.198 g/l @ 25°C
Log Partition Coefficient (octanol/H_2O)	
Henry's Law Constant	

Source: SAI (1980).

approximately 12 percent was an intermediate in the production of o-xylene, while 1 percent went into the manufacture of m-xylene. To the best of our knowledge, no production of individual xylene isomers takes place in California.

28.3 INDIRECT PRODUCTION AND EMISSIONS IN CALIFORNIA

We are unaware of indirect production mechanisms for xylenes.

28.4 INDUSTRIAL USE AND EMISSIONS

Xylenes are used industrially in three ways. First, they are feedstock or chemical intermediates for several products. Second, they are ingredients in various formulations, such as paints, coatings and adhesives; as such they may be emitted during both manufacturing and application of these formulations. Finally, o-xylene is used by itself, or in combination with other compounds, as an industrial solvent.

28.4.1 Use as Feedstock and Ingredient in Formulations

Each xylene isomer has one primary end use. Over 64 percent of o-xylene is used to manufacture phthalic anhydride. P-xylene is used chiefly in the manufacture of terephthalic acid and dimethyl terephthalate (84.5 percent), which are intermediates for polyester fiber. One hundred percent of m-xylene is used to produce isophthalic acid, which is in turn a feedstock for polyester resins.

Chevron U.S.A. operated a phthalic anhydride plant in Richmond until 1981 or 1982, when it was permanently shut down (Williams, 1986). Allied Chemical Corporation operated a phthalic anhydride facility until it ceased operations 4-5 years ago (Nauta, 1986). To the best of our knowledge, no plants in California use xylene isomers as feedstocks or chemical intermediates.

Xylenes are, however, used significantly in the state as ingredients in formulations (chiefly paints and coatings). An industrial survey conducted previously by SAIC for the ARB determined that 30.5 ± 10.3 million lb of xylenes were incorporated in formulations by California facilities in 1981 (Rogozen et al., 1985). Emissions from this use were estimated to be 341 ± 109 tons per year.

28.4.2 Solvent in Paints, Coatings, and Adhesives

The only xylene isomer used significantly as a solvent is o-xylene. A study performed for the National Paint and Coatings Association (NPCA) estimated that 464 million lb of xylene were used as paint and coating solvent in the U.S. in 1981 (Connolly et al., 1982). Of this total, over 438 million pounds were consumed solely by industrial users. We employed a method developed in the aforementioned SAIC study to apportion national use to California use. As seen in Table 28.4-1, either million worker production hours or population was used as the apportionment basis, depending upon paint and finish sub-category. By this calculation, California industries used 49.7 million pounds of xylene in paints and coatings in 1981. The SAIC study also estimated that 13,000 lb of xylene were used in that year in industrial adhesives, and that about 57 percent of the xylene used industrially is emitted. (The latter estimate is highly uncertain.) Therefore emissions from the use of xylene-containing paints, coatings, and adhesives were approximately 14,000 tons.

28.4.3 Other Industrial Solvent Uses

Ortho-xylene is also used to a fairly limited extent as a chemical and manufacturing solvent. SAIC's survey of over 6,000 industrial firms in California determined that about 2.1 ± 0.4 million lb of xylene were directly applied in 1981, and that corresponding emissions were 590 ± 112 tons.

28.4.4 Comparison With Air Quality Management District Surveys

Xylene users were identified by the South Coast and Bay Area air quality management districts through surveys conducted in 1983 and 1985, respectively. Table 28.4-2 shows the facilities identified and the emission estimates resulting from these surveys. Industrial xylene emissions in the

Table 28.4-1

O-XYLENE USE IN PAINTS AND COATINGS

Category	Product	Basis of Apportionment[a]	Apportionment Value U.S.	Apportionment Value CA	CA/U.S. Ratio	o-Xylene (million lb/yr)[b] U.S.	o-Xylene (million lb/yr)[b] CA
1	Wood Furn. & Fixt.	MPWH	391.5	45.6	0.116	45.00	5.24
2	Wood Flat Stock	MPWH	94.0	6.7	0.071	3.00	0.21
3	Metal Furn. & Fix.	MPWH	132.4	19.5	0.147	20.00	2.95
4	Containers & Closures	MPWH	94.6	15.3	0.162	20.00	3.23
5	Sheet, Strip & Coil	MPWH	53.1	8.6	0.162	18.00	2.92
6	Appliances	MPWH	180.2	4.7	0.026	15.00	0.39
7	Automotive	MPWH	7,917.0	186.0	0.024	18.00	0.45
8	Trucks and Buses	MPWH	41.3	3.7	0.090	3.00	0.27
9	Railroad	MPWH	38.5	N/A	0.000	2.00	0.00
10	Aircraft	MPWH	578.3	125.1	0.216	0.80	0.17
11	Machinery & Equipment	MPWH	1,979.3	191.2	0.097	21.00	2.03
12	Electrical Insulation	MPWH	253.5	13.5	0.053	0.00	0.00
13	Marine	MPWH	323.0	35.3	0.109	10.50	1.15
14	Paper, Film, & Foil	MPWH	53.1	8.6	0.162	5.00	0.81
15	Other Prod. Finishes	MPWH	53.1	8.6	0.162	24.00	3.89
16	Int. Archit. Coatings	SFH	65,742	7,201	0.110	1.50	0.16
17	Ext. Archit. Coatings	1000 persons	234,023	25,186	0.108	2.50	0.27
	SPECIAL PURPOSE COATINGS						
18	Auto Refinishing	1000 autos	130,364	14,274	0.109	42.00	4.60
19	Maintenance	c				23.00	2.64
20	Aerosol	c			0.104	22.00	2.29
21	Traffic Paints	1000 mi roads	3,891	173	0.044	1.00	0.04
22	Other	c				6.00	0.65
23	Thinner & Misc.	c				160.00	18.07
	TOTALS					464.30	52.44
	Industrial					438.30	49.72
	Consumer					26.00	2.72

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[a] Data sources for apportionment parameters:

MPWH (million production worker hours) -
SFH (single family homes) - U.S. Department of Housing and Urban Development (Schoun, 1986)
1000 persons - U.S. Bureau of the Census (Nerby, 1985)
1000 registered autos - U.S. Federal Highway Administration (1984)
1000 miles public roads - Motor Vehicle Manufacturers Association (Baker, 1985)

[b] Connolly et al. (1982).

[c] See Rogozen et al. (1985) for method of apportionment in these categories.

Table 28.4-2
XYLENE EMISSIONS REPORTED BY THE SOUTH COAST AND BAY AREA AIR QUALITY MANAGEMENT DISTRICTS

Firm	City	County	SCAQMD lb/yr	SCAQMD kg/yr	BAAQMD lb/yr	BAAQMD kg/yr
Able Auto Body		Alameda	-	-	T[a]	T
Advanced Structures	Monrovia	Los Angeles	4,277	1,939.7	-	-
Advanced Micro Devices		Santa Clara	-	-	U[a]	U
Allied Corporation		Contra Costa	-	-	T	T
Alta Bates Hospital		Alameda	-	-	T	T
American Can Company	Carson	Los Angeles	7,920	3,591.8	-	-
American Bentley	Irvine	Orange	2,246	1,018.6	-	-
American Can Company		Alameda	-	-	1,400	640
American Can Company		Santa Clara	-	-	U	U
A.O. Smith Corporation		Alameda	-	-	1,000	450
Ampex Corporation		San Mateo	-	-	T	T
Arnold Engineering Company	Fullerton	Orange	3,240	1,469.4	-	-
Ashland Chemical Company	Newark	Alameda	-	-	200	90
Atlantic Richfield Company	Richmond	Contra Costa	-	-	1,600	730
Ball Metal Container Group	Fairfield	Solano	-	-	U	U
Bay Area Circuits Inc.	Redwood City	San Mateo	-	-	T	T
Benson Inc.	San Jose	Santa Clara	-	-	T	T
Best Foods	San Francisco	San Francisco	-	-	T	T
Borden Chemical Company	Fremont	Alameda	-	-	T	T
Brookside Hospital	San Pablo	Contra Costa	-	-	T	T
Burke Industries, Inc.	San Jose	Santa Clara	-	-	U	U
B.W. Norton Mfg. Company, Inc.	Oakland	Alameda	-	-	4,800	2,180
C.F. Braun & Company	Alhambra	Los Angeles	3,000	1,360.5	-	-
California & Hawaiian Sugar	Crockett	Contra Costa	-	-	T	T
Carboline Company	Fremont	Alameda	-	-	T	T

Table 28.4-2 (Continued)

Firm	City	County	SCAQMD lb/yr	SCAQMD kg/yr	BAAQMD lb/yr	BAAQMD kg/yr
Carriage House Foods Division	San Jose	Santa Clara	-	-	T	T
Carter Precision Parts Inc.	Los Angeles	Los Angeles	2,376	1,077.6	-	-
Chevron Chemical Company	Richmond	Contra Costa	-	-	400	180
Chevron Research Company	Richmond	Contra Costa	-	-	11,200	5,090
Chevron USA, Inc.	Richmond	Contra Costa	-	-	200	90
Chevron USA, Inc.	Richmond	Contra Costa	-	-	16,400	7,450
Chevron USA, Inc.	Pittsburg	Contra Costa	-	-	U	U
Chevron USA, Inc.	Martinez	Contra Costa	-	-	600	270
Chevron USA, Inc.	San Francisco	San Francisco	-	-	U	U
Chevron USA, Inc.	San Jose	Santa Clara	-	-	2,400	1,090
Chevron, Oakland Airport	Oakland	Alameda	-	-	T	T
Clorox Technical Center	Pleasanton	Alameda	-	-	U	U
Community Hospital Los Gatos	Los Gatos	Santa Clara	-	-	T	T
Component Finishing Inc.	Santa Clara	Santa Clara	-	-	U	U
Cook Paint and Varnish Company	Milpitas	Santa Clara	-	-	200	90
Cybernex Corporation	San Jose	Santa Clara	-	-	T	T
Data General Corporation	Sunnyvale	Santa Clara	-	-	T	T
Dave Zedrick, Inc.	Santa Rosa	Sonoma	-	-	U	U
Del Monte Corporation	Walnut Creek	Contra Costa	-	-	T	T
DeSoto, Inc.	Berkeley	Alameda	-	-	200	90
Devoe & Reynolds	Riverside	Riverside	2,767	1,254.9	-	-
Dow Chemical Company	Pittsburg	Contra Costa	-	-	3,400	1,550
Dysan Corporation	Santa Clara	Santa Clara	-	-	T	T
E & M Spray, Inc.	Mountain View	Santa Clara	-	-	3,600	1,640
Edoco Technical Products, Inc.	Long Beach	Los Angeles	3,600	1,632.7	-	-
Engard Coatings Corporation	Huntington Beach	Orange	2,000	907.0	-	-
Exxon Company USA (Benicia)	Benicia	Solano	-	-	1,100	500

Table 28.4-2 (Continued)

Firm	City	County	SCAQMD lb/yr	SCAQMD kg/yr	BAAQMD lb/yr	BAAQMD kg/yr
Exxon Corporation	Benicia	Solano	-	-	400	180
Fafco, Inc.	Menlo Park	San Mateo	-	-	600	270
Fairchild Camera and Instruments	Mountain View	Santa Clara	-	-	43,000	19,550
Ford Aerospace & Communications	Palo Alto	Santa Clara	-	-	T	T
Forderer Cornice Works	San Francisco	San Francisco	-	-	800	360
Fuller-O'Brien Division	S. San Francisco	San Mateo	-	-	6,800	3,090
Genentech, Inc.	S. San Francisco	San Mateo	-	-	400	180
General Electric Company	San Jose	Santa Clara	-	-	400	180
General Instrument Corporation	Palo Alto	Santa Clara	-	-	1,600	730
Gillig Corporation	Hayward	Alameda	-	-	28,600	13,000
Glidden Coatings & Resins	San Francisco	San Francisco	-	-	1,600	730
Great Western Chemical Company	Richmond	Contra Costa	-	-	T	T
Harbor Universal, Inc.	San Leandro	Alameda	-	-	4,400	2,000
Harpers	Torrance	Los Angeles	24,852	11,270.7	-	-
Hewlett Packard Company	Cupertino	Santa Clara	-	-	400	180
Hewlett-Packard Co. Optoelectronics	Palo Alto	Santa Clara	-	-	400	180
Hewlett-Packard Company	Palo Alto	Santa Clara	-	-	1,400	640
Hewlett-Packard Co., Stanford	Palo Alto	Santa Clara	-	-	T	T
Hewlett-Packard Company	Sunnyvale	Santa Clara	-	-	U	U
Hewlett-Packard Company	Santa Clara	Santa Clara	-	-	3,800	1,730
Hewlett-Packard Company	Santa Rosa	Sonoma	-	-	T	T
IBM Corporation	San Jose	Santa Clara	-	-	2,000	910
Inmont Corporation	Anaheim	Orange	2,279	1,033.6	-	-
Intel Corporation	Livermore	Alameda	-	-	T	T
Intel Corporation	Santa Clara	Santa Clara	-	-	U	U
IT Corporation, Oil Reprocessing	Martinez	Contra Costa	-	-	U	U
IT Corporation, Vine Hill	Martinez	Contra Costa	-	-	U	U

Table 28.4-2 (Continued)

Firm	City	County	SCAQMD lb/yr	SCAQMD kg/yr	BAAQMD lb/yr	BAAQMD kg/yr
Jack Holland Sr. Oil Company	San Leandro	Alameda	-	-	U	U
Jones-Hamilton Company	Newark	Alameda	-	-	U	U
Kaiser Aerotech	San Leandro	Alameda	-	-	T	T
Kaiser Aluminum & Chemical	Pleasanton	Alameda	-	-	T	T
Kargo Service Center	Fremont	Alameda	-	-	3,400	1,550
Kelly-Moore Paint Co., Inc.	San Carlos	San Mateo	-	-	200	90
Koppers Co., Inc.	Richmond	Contra Costa	-	-	T	T
Kresky Signs, Inc.	Petaluma	Sonoma	-	-	3,600	1,640
L & H Paint Products	San Francisco	San Francisco	-	-	U	U
La-Z-Boy West	Redlands	San Bernardino	2,448	1,110.2	-	-
Landsea Oil Company	Martinez	Contra Costa	-	-	2,400	1,090
Lawrence Livermore National Lab	Livermore	Alameda	-	-	T	T
Lilly Industrial Coatings Inc.	Montebello	Los Angeles	6,280	2,848.1	-	-
Lockheed Missiles & Space Division	Sunnyvale	Santa Clara	-	-	200	90
Louis Roesch Company	San Francisco	San Francisco	-	-	1,400	640
Magnetic Peripherals, Inc.	Cupertino	Santa Clara	-	-	200	90
Mare Island Naval Shipyard	Vallejo	Solano	-	-	T	T
Marwais Steel Company	Richmond	Contra Costa	-	-	4,600	2,090
Memorex Corporation	Santa Clara	Santa Clara	-	-	4,200	1,910
Micrel Inc., Wafer Fabric. Div.	Sunnyvale	Santa Clara	-	-	U	U
Midland Division	Hayward	Alameda	-	-	600	270
Miracle Auto Painting	Richmond	Contra Costa	-	-	T	T
Mobil Chemical Company	Azusa	Los Angeles	8,496	3,853.1	-	-
Modern Mode Inc.	San Leandro	Alameda	-	-	U	U
Monolithic Memories, Inc	Sunnyvale	Santa Clara	-	-	38,600	17,550
Mount Zion Hospital	San Francisco	San Francisco	-	-	T	T
National Can Corporation	San Leandro	Alameda	-	-	38,200	17,360

Table 28.4-2 (Continued)

Firm	City	County	SCAQMD lb/yr	SCAQMD kg/yr	BAAQMD lb/yr	BAAQMD kg/yr
National Semiconductor Company	Santa Clara	Santa Clara	-	-	U	U
Naval Air Station Alameda	Alameda	Alameda	-	-	200	90
Nelson Tech Coatings Inc.	S. El Monte	Los Angeles	2,304	1,044.9	-	-
Northrup Corp, Nopair Division	Hawthorne	Los Angeles	56,585	25,662.1	-	-
Northwestern Venetian Supply	Oakland	Alameda	-	-	T	T
O K Radiator	Redwood City	San Mateo	-	-	T	T
Owens-Corning Fiberglass	Santa Clara	Santa Clara	-	-	T	T
Pacific Gas & Electric Company	Concord	Contra Costa	-	-	T	T
Pacific Gas & Electric Company	Pittsburg	Contra Costa	-	-	T	T
Pacific Gas & Electric Company	Antioch	Contra Costa	-	-	T	T
Pacific Gas & Electric Company	San Francisco	San Francisco	-	-	T	T
Pacific Refining Company	Hercules	Contra Costa	-	-	200	90
Pacific Refining Company	Hercules	Contra Costa	-	-	600	270
Pemaco Inc.	Los Angeles	Los Angeles	2,083	944.7	-	-
Peninsula Oil Company	Mountain View	Santa Clara	-	-	U	U
Peterbilt Motors Company	Newark	Alameda	-	-	9,200	4,180
Peterson Products	Belmont	San Mateo	-	-	800	360
Pierce & Stevens Chemical	Milpitas	Santa Clara	-	-	T	T
Polyvinyl Chemical Industry	Vallejo	Solano	-	-	T	T
PPG Ind, Coatings & Resins Div.	Torrance	Los Angeles	5,760	2,612.2	-	-
Precision Monolithics, Inc.	Santa Clara	Santa Clara	-	-	U	U
Prescolite Division of U.S.I.	San Leandro	Alameda	-	-	400	180
Radiant Color	Richmond	Contra Costa	-	-	T	T
Raychem Corporation	Menlo Park	San Mateo	-	-	U	U
Raytheon Company	Mountain View	Santa Clara	-	-	42,000	19,090
Redwood Oil Company	Santa Rosa	Sonoma	-	-	U	U
Reichhold Chemical Inc.	Azusa	Los Angeles	35,400	16,054.4	-	-

Table 28.4-2 (Continued)

Firm	City	County	SCAQMD		BAAQMD	
			lb/yr	kg/yr	lb/yr	kg/yr
Reliance Universal Inc.	Brea	Orange	5,400	2,449.0	-	-
Reynolds Metals Company	Torrance	Los Angeles	13,600	6,167.8	-	-
Rockwell Intl of Los Angeles	El Segundo	Los Angeles	11,052	5,012.2	-	-
Rockwell Intl Corporation	Newport Beach	Orange	7,160	3,247.2	-	-
Rohm and Haas California	Hayward	Alameda	-	-	T	T
Romic Chemical Corporation	E. Palo Alto	San Mateo	-	-	T	T
Safeway Spice & Dessert	Fremont	Alameda	-	-	T	T
Shell Chemical Corporation	Carson	Los Angeles	6,120	2,775.5	-	-
Shell Oil Company	Martinez	Contra Costa	-	-	6,400	2,910
Shell Oil Company, Distribution	S. San Francisco	San Mateo	-	-	1,000	450
Shell Oil Company	San Jose	Santa Clara	-	-	T	T
Sherwin-Williams Company	Emeryville	Alameda	-	-	5,400	2,450
Siemens Optoelectronics	Cupertino	Santa Clara	-	-	1,800	820
Signetics Corporation	Sunnyvale	Santa Clara	-	-	54,400	24,730
Siliconix, Incorporated	Santa Clara	Santa Clara	-	-	U	
Somitex Prints of CA Inc.	City of Industry	Los Angeles	2,016	914.3	-	-
Southern Pacific Pipe Line	Concord	San Mateo	-	-	3,200	1,450
Southern Pacific Pipe Line	San Jose	Santa Clara	-	-	8,000	3,640
SRI International	Menlo Park	San Mateo	-	-	T	T
Stanford Linear Accelerator	Menlo Park	San Mateo	-	-	T	T
Star Kist Foods Inc. Can Making	Terminal Island	Los Angeles	8,000	3,628.1	-	-
Steelcase Inc. Western Division	Tustin	Orange	3,240	1,469.4	-	-
Stewart-Filmscreen Corporation	Torrance	Los Angeles	9,450	4,285.7	-	-
Syntex (USA) Inc.	Palo Alto	Santa Clara	-	-	1,000	450
Technical Coatings Company	Santa Clara	Santa Clara	-	-	600	270
Texaco Hub Service Station	Fremont	Alameda	-	-	T	T
Texaco, Inc.	Richmond	Contra Costa	-	-	600	270

Table 28.4-2 (continued)

Firm	City	County	SCAQMD lb/yr	SCAQMD kg/yr	BAAQMD lb/yr	BAAQMD kg/yr
Texlon Corporation	Torrance	Los Angeles	2,160	979.6	-	-
Todd Shipyards Corporation	San Francisco	San Francisco	-	-	16,600	7,550
Tosco Corp, Avon Refinery	Martinez	Contra Costa	-	-	11,000	5,000
Travis AFB	Travis AFB	Solano	-	-	9,000	4,090
Tri/Valley Growers Containers	Fremont	Alameda	-	-	T	T
TRW Microwave Inc.	Sunnyvale	Santa Clara	-	-	U	U
Union Chemicals Division	Oakland	Alameda	-	-	T	T
Union Oil Co. of California	Richmond	Contra Costa	-	-	1,600	730
Union Oil Company	Rodeo	Contra Costa	-	-	11,600	5,270
United Airlines, Maintenance	S. San Francisco	San Mateo	-	-	T	T
United Can Company	Hayward	Alameda	-	-	20,000	9,090
United States Pipe & Foundry	Union City	Alameda	-	-	T	T
United Technologies, Chemicals	San Jose	Santa Clara	-	-	T	T
U.S. Army, Presidio of S.F.	San Francisco	San Francisco	-	-	T	T
U.S. DOE - Sandia National Lab.	Livermore	Alameda	-	-	T	T
U.S. Steel Corporation	Pittsburg	Contra Costa	-	-	T	T
U.S. Veterans Administration	Livermore	Alameda	-	-	T	T
U.S. Veterans Administration	Palo Alto	Santa Clara	-	-	1,200	550
U.S. Veterans Administration	San Francisco	San Francisco	-	-	T	T
Vacco Industries	S. El Monte	Los Angeles	5,544	2,514.3	-	-
Van Waters & Rogers	San Jose	Santa Clara	-	-	200	90
Varian Associates	Palo Alto	Santa Clara	-	-	200	90
Velcon Filters, Inc.	San Jose	Santa Clara	-	-	T	T
Verbatim Corporation	Sunnyvale	Santa Clara	-	-	T	T
Washington Hospital	Fremont	Alameda	-	-	T	T
Watkins-Johnson Company	Palo Alto	Santa Clara	-	-	T	T
Western Metal Decorating	Pittsburg	Contra Costa	-	-	400	180

Table 28.4-2 (continued)

Firm	City	County	SCAQMD lb/yr	SCAQMD kg/yr	BAAQMD lb/yr	BAAQMD kg/yr
Western Spray Painting	Santa Clara	Santa Clara	-	-	U	U
Westinghouse Electric Company	Sunnyvale	Santa Clara	-	-	200	90
Wickland Oil Company	Crockett	Contra Costa	-	-	1,400	640
World Airways, Inc.	Oakland	Alameda	-	-	U	U
Zilog Inc.	Campbell	Santa Clara	-	-	U	U
Total			251,655	114,129.3	452,100	205,480

Source: Summarized from emissions reported by the South Coast Air Quality Management District (Zwiacher et al., 1983) and the Bay Area Air Quality Management District (Hill, 1985).

[a] T = Emissions are 0-0.1 ton/yr; U = Xylene is used but emissions are unknown.

two districts totalled about 352 tons/yr. This value is far below the amount estimated by SAIC in 1981 (14,900 tons). The major reason for this is that the AQMD surveys, by and large, did not include emissions of xylene from paints and coatings. The Bay Area AQMD report acknowledges that, in responding to its initial screening survey, "Purchasers of paint...might not indicate usage of xylene unless the chemical itself was purchased as thinner or cleanup solvent" (Hill, 1985). Since each facility's responses to the screening survey were used to generate an individualized usage survey form, it is possible that a considerable portion of the xylene used in paints and coatings was missed in the follow-up survey. Similarly, the survey form used by the South Coast AQMD (Zwiacher et al., 1983) requests estimates of annual usage and/or emissions of xylene "used on premises." Nowhere does the form call the respondent's attention to the possibility that xylene may be present as an ingredient in a formulation. If xylene emissions through application of paints, coatings, and adhesives are ignored, then SAIC's statewide estimate of industrial xylene emissions becomes 931 ± 221 tons/yr. This value is from 2 to 3.3 times that estimated by the two AQMDs. Industrial emissions of xylene therefore are quite uncertain.

28.5 CONSUMER USE AND EMISSIONS

28.5.1 Solvent Use

Xylene emissions from consumer use of paints and coatings were estimated by using the NPCA data base mentioned in Section 28.4.2. All of the xylene emitted through applications of these materials was assumed to be emitted. As seen in Table 28.4-1, about 1,360 tons of xylene were emitted in 1981. SAIC's previous organic solvent inventory research (Rogozen et al., 1985) determined that xylenes are present in nail polish, spot removers, carburetor cleaners, and engine cleaners. Emissions from these formulations were estimated to be 11,000 lb (5.5 tons) in 1981.

28.5.2 Gasoline Consumption

Among the largest sources of xylenes released to the atmosphere are automotive related uses, since over 92 percent of all mixed xylenes are blended into gasoline. Xylene is emitted through evaporation from gasoline marketing, evaporation from automobiles, and automotive exhaust.

To calculate xylene emissions from gasoline marketing, we assumed an emission factor of 0.004735 lb hydrocarbon lost per lb gasoline consumed, and a xylene (all isomers) mass fraction of 0.0031 in gasoline vapor (SAI, 1980). According to the California Energy Resources, Conservation and Development Commission, 1.1 x 10^{10} gal of gasoline were sold in California in 1985 (Trenschel, 1986). Emissions were therefore (1.18 x 10^{10} gal/yr)(5.87 lb/gal)(0.0031)(0.004735) = 1,017,000 lb/yr (508 tons/yr).

Xylene emissions from automotive evaporation were estimated using an emission factor of 0.83 g/mi hydrocarbon evaporative loss (SAI, 1980) and 171.2 billion miles driven by California motorists in 1985 (Avlani, 1986). Emissions from this source were (171.2 x 10^9 mi/yr)(0.83 g/mi)(0.0031)/(453.6 g/lb) = 971,000 lb/yr (486 tons/yr).

Xylene emissions from automotive exhaust were estimated by assuming an emission factor of 2.37 g/mi of hydrocarbons in the exhaust (Sigsby et al., 1984), and 3.4 percent xylene in the exhaust hydrocarbons (SAI, 1980). Thus emissions in 1985 were (171.2 x 10^9 mi/yr)(2.37 g/mi)(0.034)/(453.6 g/lb) = 30,413,000 lb/yr (15,206 tons/yr).

Xylene emissions from gasoline use, therefore, totaled more than 16,000 tons/yr in 1985. With the recent reduction in the amount of lead allowed as an octane booster in gasoline, refineries will increasingly be turning toward aromatics to replace lead (Savage, 1986). The most likely aromatics to be used as a substitute are toluene and xylenes. Pressure to use these low vapor pressure aromatics will also come from EPA regulations to cut evaporative emissions from gasoline by lowering the overall gasoline vapor pressure rather than by installing vapor-recovery systems on automobiles. Therefore, emissions of xylene from automotive sources may increase.

28.6 EMISSION SUMMARY

Table 28.6-1 summarizes our estimates of xylene emissions in California. No manufacturers of isolated mixed xylenes are located in the state; we do not presently know whether any manufacturers of non-isolated xylenes have facilities within the state. No California manufacturing plants use individual xylene isomers as feedstocks. Emissions from industrial formulation of xylene-containing products; use of paints, coatings and adhesives; and direct use of xylene as a solvent are about 14,900 tons per year. This value exceeds considerably the combined total of estimates developed by the Bay Area and South Coast air quality management districts; however, the latter value may have ignored emissions from use of xylene in paints and coatings. In any event, industrial emissions are uncertain. Our estimate of emissions from consumer use of paints, coatings, various other consumer products, and gasoline is about 17,600 tons per year. Automotive-related emissions, which account for about half of the statewide total, are expected to increase as aromatics replace lead in gasoline. Total xylene emissions in California are estimated to be about 32,500 tons per year.

28.7 SUMMARY OF AMBIENT CONCENTRATION DATA

A substantial body of information is available concerning ambient levels of xylenes. Much of the data published prior to 1980 have been reviewed in the document, The Alkylbenzenes (NAS, 1980). More recent data are also discussed in this section, with emphasis on California.

Table 28.7-1 summarizes available data on xylene concentrations in California. Concentrations of xylenes in downtown Los Angeles air have been measured since 1966 (Lonneman et al., 1968) and as recently as 1981 (Grosjean and Fung, 1984). Data for other locations in the Los Angeles area are available since 1967 (Altschuller et al., 1971) and as recently as 1984 (Singh et. al., 1985). There appears to be no trend in ambient levels of xylenes during 1966-1984. There is no long-term monitoring program for individual hydrocarbons, and the data listed in Table 28.7-1 are not suitable for trend

Table 28.6-1
SUMMARY OF CALIFORNIA XYLENE(S) EMISSIONS

Source	Tons
Emissions from Industrial Use	
Feedstock	0
Ingredient in Formulations	341 ± 109
Use of Paints, Coatings and Adhesives	14,000
Direct Industrial Solvent Use	590 ± 112
Total Industrial Emissions	14,931
Emissions from Consumer Use	
Use of Paints, Coatings and Adhesives	1,360
Other Consumer Products	6
Gasoline Marketing	508
Gasoline Evaporation from Automobiles	486
Automobile Exhaust	15,206
Total Consumer Use Emissions	17,566
Total Statewide Emissions	32,497

Table 28.7-1

AMBIENT LEVELS OF XYLENES AT CALIFORNIA LOCATIONS

(Concentrations in ppb)

Location	Year	Ortho	Meta	Para	Meta + Para	Reference
Los Angeles	1966	8	16	6	-	Lonneman et al., 1968
Los Angeles	1961	6.5	12	15	-	Altschuller et al., 1971
Azusa	1967	3	5.5	2	-	
Los Angeles	1968	11	13	12	-	Kopczynski et al., 1972
Los Angeles	1973	6	-	-	14	Calvert, 1976
Azusa	1975	2.9	-	-	8.6	CARB, 1976
El Monte	1975	3.2	-	-	7.0	
Long Beach	1975	1.3	-	-	3.5	
Upland	1977	1.7	-	-	4.5	Pellizzari, 1979
Los Angeles	1979	1.9	-	-	4.6	Singh et al., 1981
Oakland	1979	0.8	-	-	1.5	
Los Angeles	1981	4-13[a]	-	-	11-45[a]	Grosjean and Fung, 1984
Riverside	1980	1.1	-	-	2.2	Singh et al., 1985
Downey	1984	4.2	-	-	10.2	

[a] Range of concentrations in 6-9 a.m. samples.

analysis since different investigators used different sampling periods and frequencies. It has been suggested (e.g. NAS, 1980; Singh et al., 1985) that ambient levels of benzene and toluene have decreased substantially since the mid-1960s, due to implementation of emission control measures. Such a decrease is not apparent for the xylenes. This may reflect the recent changes in fuels composition, including higher aromatic hydrocarbon content in unleaded gasolines (see Section 28.5-2).

Diurnal variations in ambient xylene levels (e.g. Lonneman et al., 1968) correlate well with those of carbon monoxide, as expected since automobile exhaust is a major component of the total xylene emissions.

Data for other urban areas in the U.S. (Brodzinski and Singh, 1983; Singh et al., 1985) and in other countries are consistent with those obtained in California, both in terms of xylene concentrations (see Table 28.7-2) and traffic-related diurnal variations (Clark et al., 1984). Xylene levels in most urban areas are typically in the range 1-10 ppb, as compared with about 3-20 ppb in the Los Angeles area.

Data for xylene concentrations measured at "remote" locations in continental and oceanic air are compiled in Table 28.7-3. The values for continental sites are 0.002-0.140 ppb (2-140 ppt) for o-xylene and 0.03-0.33 ppb for the sum of m- and p-xylene. The higher values within these ranges reflect long-range transport of polluted air from urban areas in the mid-latitudes (e.g. Roberts et al., 1984) as well as contribution from biomass burning in the tropical regions (e.g. Greenberg et al., 1985). Biomass burning (fires) is a major source of reactive hydrocarbons in the global troposphere (e.g. Greenberg et al., 1984, Crutzen et al., 1985). Xylene values in oceanic air may be as low as $\leq$ 1 ppt (Eichmann et al., 1980). Higher values may reflect emissions from the ocean in active upwelling zones (e.g. Greenberg and Zimmerman, 1984) as well as evaporation of aromatic hydrocarbons from contaminated water in major shipping lanes (Greenberg and Zimmerman, 1984; Nutmagul and Cronn, 1985).

Because more data on ambient levels of xylenes and other aromatic

Table 28.7-2

AMBIENT LEVELS OF XYLENES AT SELECTED URBAN LOCATIONS

(Concentrations in ppb)

Location	Year	Ortho	Meta	Para	m+p	Reference
Zurich	1971	9.3	9.0	21	-	Grob and Grob, 1971
The Hague	1975	3.1	-	-	12.4	Burghardt and Jeltes, 1975
Berlin	1975	-	-	-	18.1	Seifert and Ulrich, 1978
	1976	-	-	-	13.6	
Paris	1973	0.6	-	-	1.5	Raymond and Guiochon, 1974
Johannesburg	1977	1.6	-	-	4.5	Louw et al., 1977
Pretoria	1977	1.8	-	-	4.0	
Durban	1977	1.3	-	-	4.0	
Sidney	1980	1.5	-	-	1.3	Nelson and Quigley, 1982
London	1982	1.2	-	-	2.8	Clark et al., 1984
	1983	0.8	-	-	2.3	
Delft	1980	0.7	1.4	0.6	-	Guicherit and Schulting, 1985
Tokyo	1980	0.5	0.8	0.4	-	Uno et al., 1985
	1981	0.8	1.0	0.7	-	
Helsinki	1979	7	10	-	-	Hasanen et al., 1981
Leningrad	1976	+[a]	+	+	-	Ioffe et al., 1977
	1977[b]	+	+	+	-	Ioffe et al., 1979
Phoenix, AZ	1979	1.8	-	-	4.2	Singh et al., 1985
Houston, TX	1980	1.3	-	-	3.8	Singh et al., 1985
St. Louis, MO	1980	0.3	-	-	1.0	Singh et al., 1985
Denver, CO	1980	1.3	-	-	2.9	Singh et al., 1985
	1984	0.6	-	-	1.9	Singh et al., 1985
Staten Island, NY	1984	2.6	-	-	2.6	Singh et al., 1985

[a] Identified, concentration not reported.

[b] Also Baku, Tbilisi, Kemerovo, Murmansk and Tashkent.

Table 28.7-3
XYLENE CONCENTRATIONS IN NONURBAN AIR
(Concentrations in ppt)

Category	Location	o	m	p	m+p	o+m+p	Reference
Oceanic	Loop Head, Ireland	-	-	-	-	2.7	Eichmann et al., 1979
Oceanic	Loop Head, Ireland	0.95	1.32	0.37	-	-	Eichmann et al., 1980
	Cape Grim, Tasmania	0.02	0.17	0.02	-	-	
Oceanic	Pacific Ocean, 0-20^{o}N	10-770	-	-	10-310	-	Greenberg and Zimmerman, 1984
Continental	Brazil Surface	80	-	-	120	-	
	Treetop-2 km	140	-	-	-	-	
	2 km-tropopause	80	-	-	80	-	
Continental	Kenya	10-120	-	-	30-330	-	Greenberg et al., 1985
Continental	Niwot Ridge, CO	2-55	-	-	-	-	Roberts et al., 1984
Oceanic	Pacific Ocean, 0-42^{o}N	14±6	-	-	25±12	-	Nutmagul and Cronn, 1985
	Pacific Ocean, 0-30^{o}S	7±3	-	-	13±5	-	

hydrocarbons have become available in recent years, and the only important removal process for these hydrocarbons in the troposphere is their reaction with OH, several recent studies of ambient levels of aromatic hydrocarbons have included calculations of the corresponding OH radical concentrations. Results of these calculations are compiled in Table 28.7-4. Conversely, air mass transport times have been estimated from the measured hydrocarbon concentrations and assuming an "average" OH concentration in the atmosphere (e.g. Nelson and Quigley, 1983; Nutmagul and Cronn, 1985). A systematic application of these analyses to hydrocarbon data in California air would be most useful.

28.8 ATMOSPHERIC CHEMISTRY

28.8.1 In-Situ Formation

No reactions are known to produce xylenes in the atmosphere.

28.8.2 Removal Processes

Photolysis, reaction with ozone and reaction with the nitrate radical are of negligible importance in the atmosphere. Xylenes react rapidly with the hydroxyl radical (Perry et al., 1977) and this reaction constitutes their only important removal process in the atmosphere:

o-xylene: $k_{OH} = 1.4 \times 10^{-11}$ cm^3 molecule^{-1} sec^{-1}

m-xylene: $k_{OH} = 2.4 \times 10^{-11}$ cm^3 molecule^{-1} sec^{-1}

p-xylene: $k_{OH} = 1.5 \times 10^{-11}$ cm^3 molecule^{-1} sec^{-1}

The reaction of OH with xylenes involves two pathways, one of addition to the aromatic ring (major) and one of H-atom abstraction from the

Table 28.7-4

ESTIMATES OF OH CONCENTRATIONS IN THE ATMOSPHERE FROM AMBIENT LEVELS OF AROMATIC HYDROCARBONS

Reference	HC Used, Ratio to Benzene	OH, molecules cm^{-3}
Roberts et al., 1984 (Niwot Ridge, CO, remote continental)	toluene	$1.2 \pm 0.6 \times 10^6$
	ethyl benzene	$1.0 \pm 0.8 \times 10^6$
	o-xylene	$0.48 \pm 0.8 \times 10^6$
Calvert, 1976 (Los Angeles, CA, urban)	[a]	$2.5 \pm 2.0 \times 10^6$
Singh et al., 1985 (Downey, CA, urban)	toluene	$\geq 3.1 \times 10^6$
	ethylbenzene	$\geq 2.8 \times 10^6$
	m + p-xylene	$\geq 2.0 \times 10^6$
	o-xylene	$\geq 2.3 \times 10^6$
	ethyltoluene	$\geq 3.4 \times 10^6$
	1, 2, 4-trimethylbenzene	$\geq 2.8 \times 10^6$
	1, 3, 5-trimethylbenzene	$\geq 1.9 \times 10^6$
	Average	$\geq 2.6 \pm 0.6 \times 10^6$

[a] Several ratios, none involving aromatic hydrocarbons (e.g. 1-butene/acetylene, n-pentane/acetylene, etc.).

methyl substituents:

$$CH_3\text{-}C_6H_4\text{-}CH_3 + OH \rightarrow CH_3\text{-}\dot{C}_6H_4(OH)\text{-}CH_3 \quad \text{(addition)}$$

$$\rightarrow \dot{C}H_2\text{-}C_6H_4\text{-}CH_3 + H_2O \quad \text{(abstraction)}$$

Laboratory studies of the atmospheric reactions of the xylenes are listed in Table 28.8-1 for each xylene isomer. Early studies (Altschuller et al., 1962; Altschuller and Cohen, 1963; Kopzynski, 1964) yielded qualitative observations of aromatic ring opening (formaldehyde and peroxyacetylnitrate, $CH_3C(O)OONO_2$, as reaction products) and of pathways consuming significant amounts of NO_2. More recent studies involved the identification of major reaction products and of the corresponding reaction pathways. Listed in Tables 28.8-2 and 28.8-3 are the reaction products of o- and m-xylene, respectively, and their yields as measured in the recent study of Gery et al. (1986). Major features of the OH-xylene reaction mechanism are summarized below.

- The minor abstraction pathway leads to tolualdehydes and methylbenzylnitrates (Figure 28.8-1). The major addition pathway involves reaction of the xylene-OH adduct with NO_2 to form nitroxylenes, and with O_2 (addition) to form a xylene OH-O_2 adduct. These pathways are shown in Figures 28.8-2 and 28.8-3 for o-xylene and m-xylene, respectively. The adduct may decompose (aromatic ring opening) to yield the dicarbonyl products glyoxal (CHOCHO, all three xylenes), methyl glyoxal (CH_3COCHO, all three xylenes) and biacetyl ($CH_3COCOCH_3$, o-xylene only). The adduct may also undergo reactions that do not result in ring opening, e.g. to form quinones, as is shown in Figures 28.8-2 and 28.8-3.

The relative importance of all the competing pathways is still the object of debate, not only for xylenes but for all aromatic hydrocarbons. From kinetic data (Perry et al., 1977), the abstraction pathway accounts for 20, 4, and 7 percent of the total OH reaction for o-, m-, and p-xylene, respectively. Estimates from products studies are somewhat different, e.g. 18.6 $\pm$ 8.3 percent for o-xylene and 9.4 $\pm$ 2.1 percent for m-xylene (Gery et

Table 28.8-1

LABORATORY STUDIES OF ATMOSPHERIC CHEMISTRY OF XYLENES

Reference	Xylene isomer		
	ortho	meta	para
Altschuller et al., 1962	+	+	+
Altschuller and Cohen, 1963	+	+	+
Kopczynski, 1964	+	+	+
Perry et al., 1977[a]	+	+	+
Darnall et al., 1979[b]	+		
Tagaki et al., 1980	+		
Kenley et al., 1981			+
Atkinson et al., 1983[b]	+		
Shepson et al., 1984	+		
Tuazon et al., 1984[c]		+	+
Bandow et al., 1985	+	+	+
Tuazon et al., 1986[c]	+	+	+
Gery et al., 1986	+	+	

[a] OH rate constants, reaction products not studied.

[b] Study limited to biacetyl yield.

[c] Study limited to dicarbonyl yields (glyoxal and methyl glyoxal from m-xylene and p-xylene, and glyoxal, methyl glyoxal and biacetyl from o-xylene).

Table 28.8-2

PRODUCTS AND YIELDS IN THE PHOTOOXIDATION OF M-XYLENE

Conditions			
Residence Time (min.)	7.79	19.37	22.24
Dark exit concentration (ppmC)	136.12	151.50	222.64
Lights-on exit concentration (ppmC)	128.08	140.97	203.77
Δ[*m*-xylene] (ppmC)	8.04	10.53	18.87
Δ[*m*-xylene] (percent)	5.91	6.95	8.48
Inlet [NO_X] (ppm)	7.9	n.a.	8.2
[HC]/[NO_X] (ppmC/ppm)	17.8	n.a.	28.1
Chamber Temperature (Kelvin)	305.1	304.0	302.9
Product Distribution (Percent of Reacted Carbon)			
Carbon Monoxide	6.1	6.0	4.5
Formaldehyde	2.9	1.2	3.6
Glyoxal	3.1	1.7	2.1
Methylglyoxal	20.6	10.0	13.0
Biacetyl	—	—	—
Peroxyacetylnitrate	n.a.	0.6	1.0
m-Methylbenzyl Nitrate	1.1	0.8	0.4
m-Tolualdehyde	18.1	8.4	6.8
2-Nitro-*m*-xylene	0.0	0.0	0.0
4-Nitro-*m*-xylene	1.5	3.2	1.5
5-Nitro-*m*-xylene	0.6	1.4	0.6
2,6-Dimethyl-*p*-benzoquinone	13.8	8.4	5.7
2,4-Dimethylphenol	0.2	0.3	0.2
6-Nitro-2,4-dimethylphenol	11.7	9.8	7.7
2,6-Dimethylphenol	0.2	0.7	0.5
4-Nitro-2,6-dimethylphenol	7.6	6.3	5.0
3,5-Dimethylphenol	0.0	0.0	0.0
Unidentified Gas Phase Species (approx.)	11.4	9.7	8.9
Aerosol	1.7	5.6	1.6
Percent of Reacted Carbon Detected	100.5	73.9	63.0

Table 28.8-3

PRODUCTS AND YIELDS IN THE PHOTOOXIDATION OF O-XYLENE

Conditions		
Residence Time (min.)	10.78	22.55
Dark exit concentration (ppmC)	188.43	194.17
Lights-on exit concentration (ppmC)	183.61	180.68
Δ[*o*-xylene] (ppmC)	4.82	13.49
Δ[*o*-xylene] (percent)	2.56	6.95
Inlet $[\mathrm{NO_x}]$ (ppm)	8.2	8.0
$[\mathrm{HC}]/[\mathrm{NO_x}]$ (ppmC/ppm)	23.3	25
Chamber Temperature (Kelvin)	303.5	300.2
Product Distribution (Percent of Reacted Carbon)		
Carbon Monoxide	n.a.	1.5
Formaldehyde	4.8	2.2
Glyoxal	3.1	2.0
Methylglyoxal	12.2	9.7
Biacetyl	8.5	7.2
Peroxyacetylnitrate	1.2	0.9
o-Methylbenzyl Nitrate	2.1	0.7
o-Tolualdehyde	19.2	11.7
3-Nitro-*o*-xylene	1.2	0.8
4-Nitro-*o*-xylene	6.6	5.1
2,3-Dimethyl-*p*-benzoquinone	3.3	3.1
2,3-Dimethylphenol	3.8	2.8
6-Nitro-2,3-dimethylphenol (tentative)	2.7	1.5
4-Nitro-2,3-dimethylphenol	2.7	1.5
3,4-Dimethylphenol	0.9	1.1
2- or 5-Nitro-3,4-dimethylphenol	0.4	0.3
6-Nitro-3,4-dimethylphenol	1.5	1.0
Unidentified Gas Phase Species (approx.)	13.7	11.5
Aerosol	n.a.	n.a.
Percent of Reacted Carbon Detected	87.9	64.5

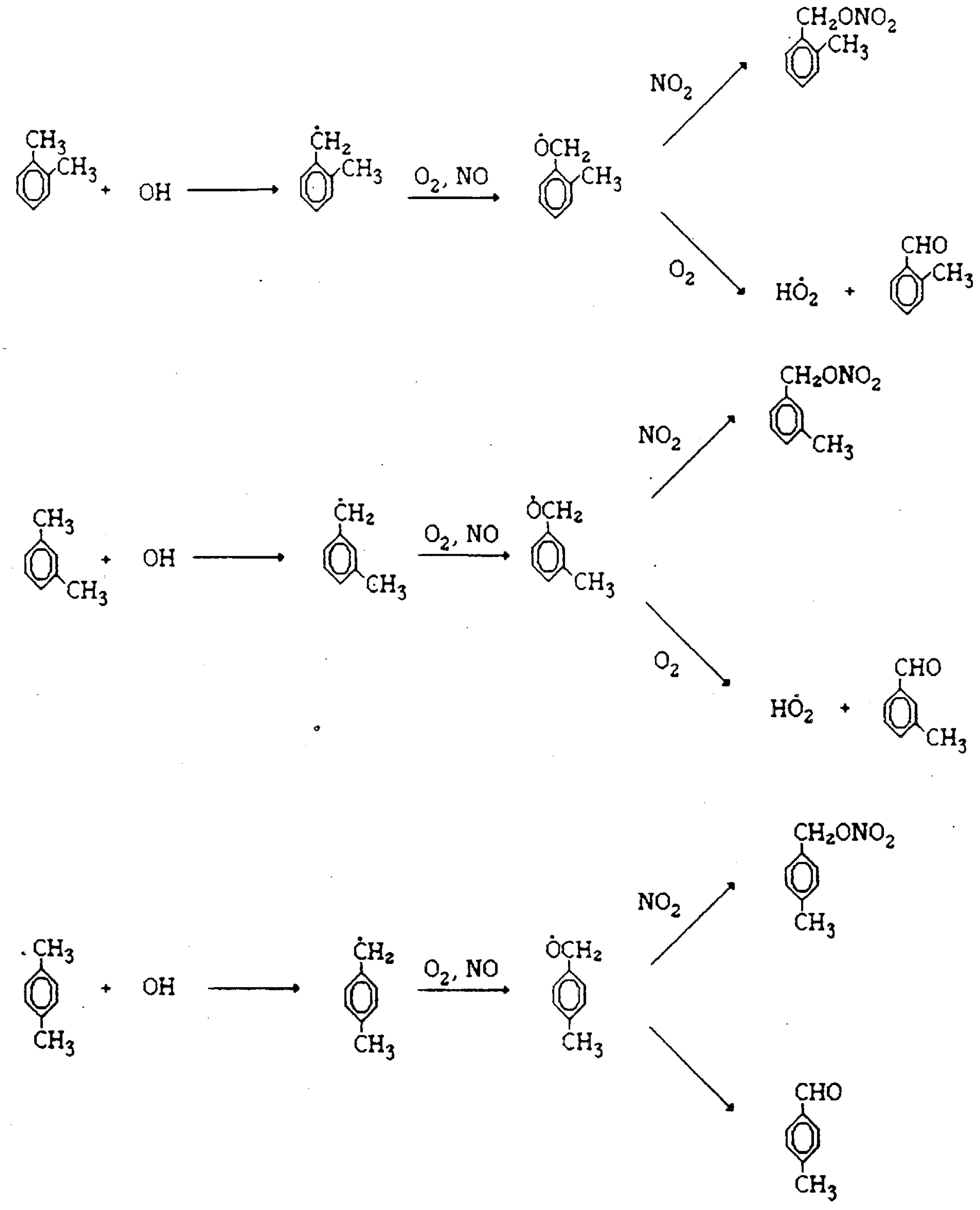

Figure 28.8-1. OH-Xylene Abstraction Pathway.

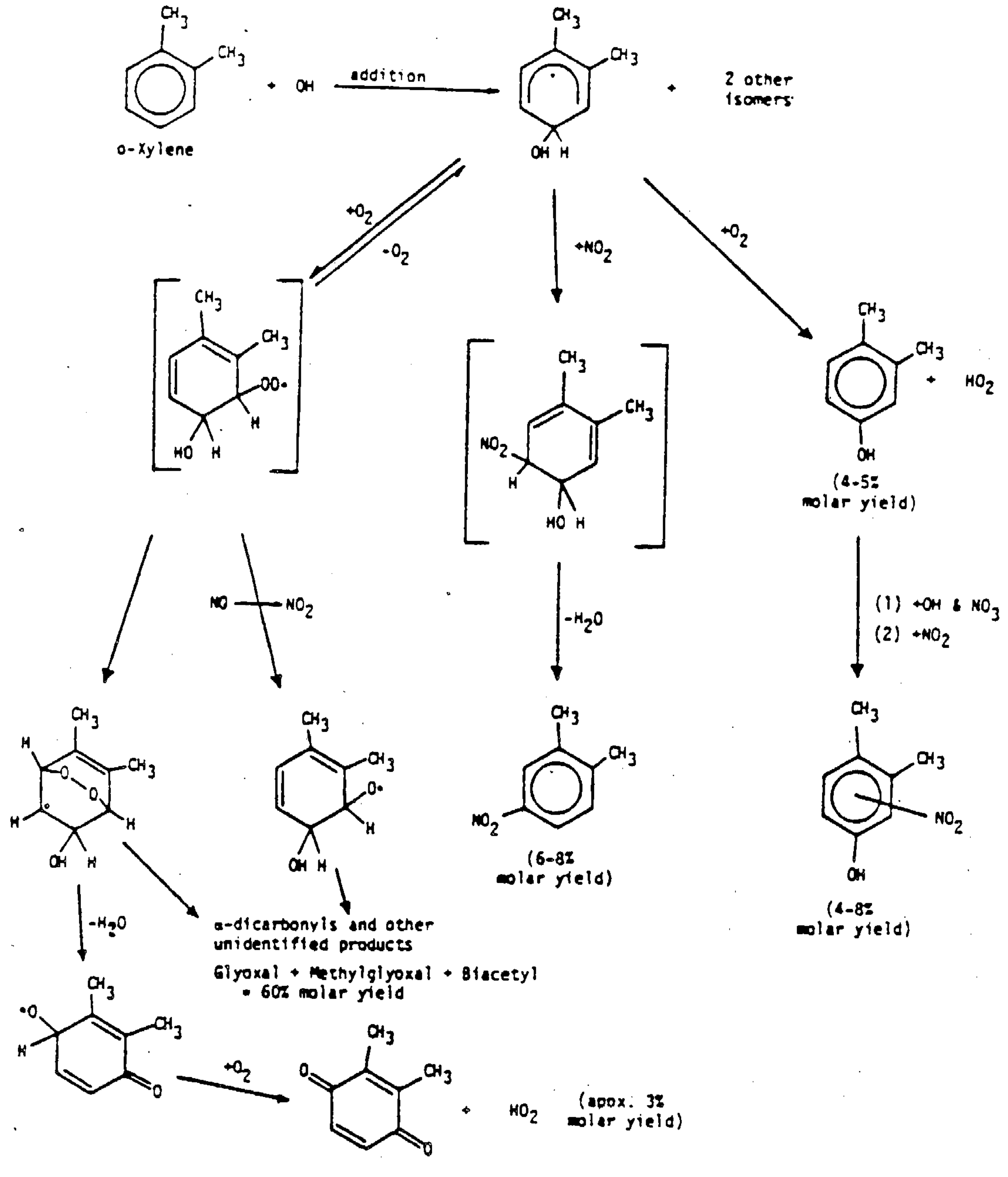

Figure 28.8-2. Hydroxyl Radical-o-Xylene Addition Reaction Mechanism (Gery et al., 1986).

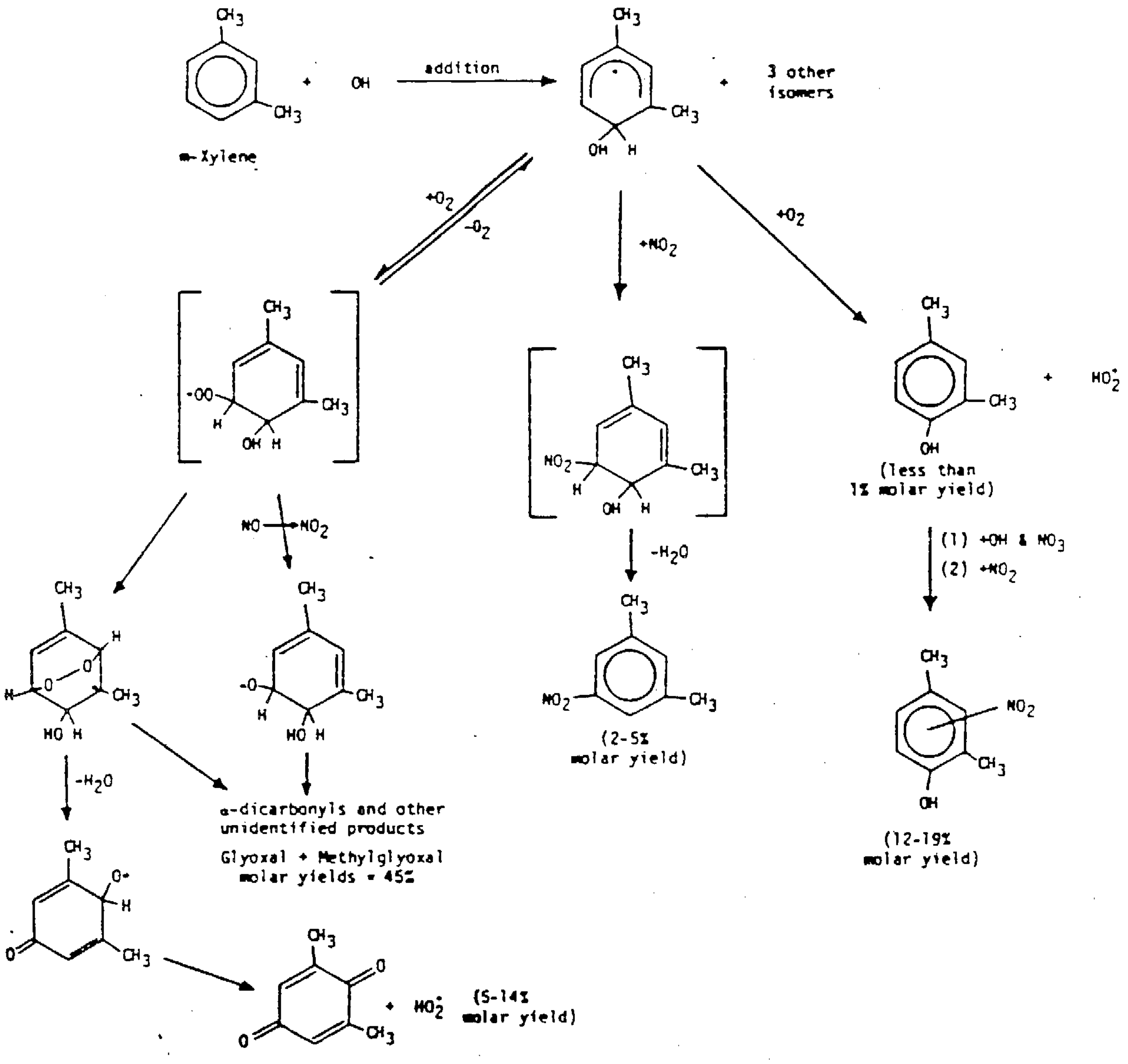

Figure 28.8-3. Hydroxyl Radical-m-Xylene Addition Reaction Mechanism (Gery et al., 1986).

al., 1986). A large fraction of the OH-xylene adduct is not accounted for by measured product yields. Reactions of the adduct with O_2 (abstraction) and with NO_2 to yield the "ring-conserving" products dimethylphenols and nitroxylenes, respectively, account for $\geq$ 15 percent of the total adduct reaction for o-xylene and $\geq$ 25 percent for m-xylene (Gery et al., 1986). The dicarbonyl yields (Table 28.8-4) vary somewhat among investigators. These yields provide lower limits for reactions of the xylene-OH-O_2 adduct. Adding all measured gas phase and aerosol product yields (after correction for their own removal processes, i.e. reaction with OH and photolysis) still leaves about 20-30 percent of reacted xylene not accounted for. Much of this "missing" chemistry involves as yet unidentified reactions of the xylene-OH-O_2 adduct.

Subsequent reactions of the "first generation" xylene-OH products must also be considered in the context of atmospheric removal processes. The dicarbonyls, glyoxal, methyl glyoxal and biacetyl are rapidly removed by reaction with OH or by photolysis (Plum et al., 1983; Grosjean, 1985). Cresols react rapidly with OH and NO_3 to form nitrocresols and other products (Grosjean, 1984, 1985). Accordingly, dimethylphenols are expected to yield dimethylnitrophenols, as has indeed been recently observed by Gery et al. (1986) for several dimethylphenol isomers. No OH or NO_3 reaction rate constants are available for the dimethylphenols. Taking those of cresols as lower limits, we estimate $k_{OH} \geq 5\text{-}7 \times 10^{-11}$ cm^3 $molecule^{-1}$ sec^{-1} and $k_{NO_3} \geq 1.2 \times 10^{-11}$ cm^3 $molecule^{-1}$ sec^{-1}. During daytime, dimethylphenols will react with OH about 5 times faster than xylenes do. They will also react rapidly with NO_3 at night. These reactions, along with scavenging by rain and fog (see Chapter 24), will result in a rapid removal of dimethylphenols from the atmosphere.

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Table 28.8-4

DICARBONYL YIELDS FROM o, m AND p-XYLENE

	Glyoxal	Methylglyoxal	Biacetyl	Reference
o-xylene	-	-	0.18 ± 0.04	Darnall et al., 1979
	-	-	0.26 ± 0.10	Tagaki et al., 1980
	-	-	0.14 ± 0.02	Atkinson et al., 1983
	0.08 ± 0.04	0.23 ± 0.03	0.10 ± 0.02	Bandow et al., 1985
	0.09 ± 0.01	0.25 ± 0.02	-	Tuazon et al., 1986
	0.112	0.340	0.158	Gery et al., 1986
m-xylene	0.13 ± 0.03	0.42 ± 0.05	0[a]	Bandow et al., 1985
	0.10 ± 0.02	0.26 ± 0.03	0[a]	Tuazon et al., 1984
	0.09 ± 0.01	0.32 ± 0.01	0[a]	Tuazon et al., 1986
	0.086	0.375	0[a]	Gery et al., 1984
p-xylene	0.24 ± 0.02	0.12 ± 0.02	0[a]	Bandow et al., 1985
	0.12 ± 0.02	0.11 ± 0.01	0[a]	Tuazon et al., 1984
	0.22 ± 0.04	0.10 ± 0.03	0[a]	Tuazon et al., 1986

[a] Biacetyl does not form from m- and p-xylene.

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29.0

SELECTION OF COMPOUNDS FOR PHASE II

29.1 RANKING APPROACH

In deciding which Level 2 compounds or compound classes to recommend for Phase II, we were guided by Section 39660(f) of the California Health and Safety Code, which requires evaluation and regulation on the basis of "factors related to the risk of harm to public health, amount or potential amount of emissions, manner of usage of the substance in California, persistence in the atmosphere, and ambient concentrations in the community." Uncertainties in the available information were also to be taken into account. Because no formal procedure for defining and using the "factors" required by Section 39660(f) was available, we developed one of our own.

As is clear from the dossiers presented in Chapters 4 through 28, data on the use, emissions, and ambient concentrations of a significant portion of the Level 2 potential toxic air contaminants are lacking and/or highly uncertain. This absence of data precludes use of quantitative scoring systems such as the one used in a previous ranking of carcinogens in California (Margler et al., 1979) or the U.S. Environmental Protection Agency's Hazardous Air Pollutant Prioritization System (Smith and Fingleton, 1982). Instead, we used a three-step semi-quantitative approach, which takes into account both the information obtained in Phase I and the uncertainty therein. Our procedure was to:

(1) Rank compounds according to emissions, uncertainty in emissions, and uncertainty in ambient concentration data;

(2) Make a preliminary selection on the basis of the first ranking;

(3) Add compounds for which we have at least some ambient concentration data, which form in the atmosphere, and which have substantial atmospheric persistence or toxic degradation products.

29.2 RANKING BY EMISSIONS AND AMBIENT CONCENTRATION DATA

Tables 29.2-1 and 29.2-2 summarize our findings regarding use, emissions, and ambient concentrations of the Level 2 potential toxic air contaminants. The data in these tables were used for the first step of the ranking exercise.

In ranking the compounds according to their emissions and ambient concentrations, we judged emissions to be more important than uncertainty in emissions, and uncertainty in emissions to be more important than uncertainty in ambient concentration data. As will be discussed in a moment, each of the three criteria was rated "high," "medium," or "low" for each compound. There were therefore 27 combinations of ratings for the 3 criteria. These combinations were ranked in descending order, starting with "high" emissions + "high" uncertainty in emissions + "high" uncertainty in ambient data, and ending with "low" emissions + "low" uncertainty in emissions + "low" uncertainty in ambient data. The first three columns of Table 29.2-3 show how the 27 combinations were ranked. Each compound was then assigned to the combination corresponding to its rating against the three criteria.

Emissions were rated as follows for each compound:

High = Over 1,000 tons/yr
Medium = 100 - 1,000 tons/yr
Low = Less than 100 tons/yr

Uncertainty in emissions was rated qualitatively on the basis of the methods used to develop the emission estimates. The only compounds for which uncertainty in emissions was rated low were chloroprene and hexachlorocyclopentadiene; we are fairly certain that these compounds are not produced or used in California. The uncertainty in emissions of glycol ethers and xylenes was considered to be "medium," as these compounds were subject of a previous statewide emission inventory study for the ARB (Rogozen

Table 29.2-1

SOURCES AND EMISSIONS OF LEVEL 2 POTENTIAL TOXIC AIR CONTAMINANTS IN CALIFORNIA

	Produced in CA	Indirect Sources[a]	Industrial Use	Consumer Use	Emissions (Tons/yr) Low	Emissions (Tons/yr) High	Uncertainty in Emissions
Acetaldehyde	No	SC,M	No	Low	7,800	12,000	High
Acrolein	No	SC,M	No	No	1,800	4,100	High
Acrylonitrile	No	No	Wide	No	0	3	High
Allyl Chloride	No	No	Narrow	No	0	1	High
Benzyl Chloride	No	No	Narrow	Low?	1	1	High
Monochlorobenzene	No	SC	Wide	Wide?	2	?	High
Chloroprene	No	No	No	No	None		Low
Cresols	Yes	No	Wide	Wide	870	870	High
Chlorobenzenes	No	No?	Wide	Wide	3,000	3,000	High
Dialkyl Nitrosamines	No	SC,M	No	No	Unknown		High
1,4-Dioxane	No	No	Wide	Low	200	600	Medium
Epichlorohydrin	No	No	Narrow	Low	0	1	High
Glycol Ethers	No	No	Wide	Wide	12,400	13,850	Medium
Hexachlorocyclopentadiene	No	No	No	No	None		High
Maleic Anhydride	No	No	Narrow	No	8	8	High
Manganese	No	SC,M	Wide	Low?	56	84	High
Methyl Bromide	No	No	Wide	Low	3,500	?	Medium
Mercury	Small	SC,Geoth	Wide	Wide	1	2	High
Nitrobenzenes	No	No	Narrow	Unknown	Unknown		High
Nitrosomorpholine	No	No	Low?	Low?	Unknown		High
Phenol	Yes	SC,M	Narrow	Low	514	514	Medium
Phosgene	No	No	No	No	None		High
Propylene Oxide	No	No	Narrow	Low?	160	160	Medium
Vinylidene Chloride	No	No	Narrow	No	4	4	Medium
Xylenes	No?	No	Wide	Wide	32,500	32,500	Medium

[a] SC = stationary combustion source, M = mobile source, Geoth = geothermal power plants.

Table 29.2-2

SUMMARY OF AMBIENT GAS-PHASE CONCENTRATION DATA FOR CALIFORNIA

Level 2 Compound	California Concentrations	Dates	Size of Data Base	Comments
Acetaldehyde	3 - 39 ppb	1980-1981	Extensive	
Acrolein	Up to 14 ppb	1961-1968	Limited	Means 4 - 7 ppb in CA
Acrylonitrile	No data	-	None	Mean 12 ppb, max 110 ppb near sources in other states
Allyl Chloride	No data	-	None	
Benzyl Chloride	No data	-	None	
Monochlorobenzene	Up to 21 ppb	1979-1981	Limited	Means 0.004 - 3.4 ppb in CA; concentrations vary widely among investigators; some discrepancies within data sets
Chloroprene	No data	-	None	
Cresols	Up to 29 ppb	1979	14 samples	O-cresol measured near point source at 1 point (mean = 6.0 ppb); no CA data for m- or p-cresol; in OR, mean ambient o-cresol 0.016 ppb, m+p-cresol 0.03 ppb
Chlorobenzenes				
o-DCB	Up to 310 ppt	1979-1983	Limited	Means 13 - 130 ppt; higher values may have been near sources; some discrepancies within data sets; higher values in U.S. urban areas outside CA
m-DCB	Up to 150 ppt	1983	Limited	Means 4 - 77 ppt; higher values may have been near sources; some discrepancies within data sets; higher values in U.S. urban areas outside CA

Table 29.2-2 (Continued)

SUMMARY OF AMBIENT GAS-PHASE CONCENTRATION DATA FOR CALIFORNIA

Level 2 Compound	California Concentrations	Dates	Size of Data Base	Comments
Chlorobenzenes (continued)				
p-DCB	No data	-	None	
Dialkyl Nitrosamines	0 - 160 ppt	1978	Limited	Data for dimethylnitrosamine only; means 0 - 31 ppt in 15 cities in South Coast Air Basin
Dimethylnitrosamine	20 - 360 ppt	1978	One set	Dimethylnitrosamine in Contra Costa County
1,4-Dioxane	No data	-	None	
Epichlorohydrin	No data	-	None	
Glycol Ethers	No data	-	None	
Hexachlorocyclopentadiene	No data	-	None	
Maleic Anhydride	No data	-	None	
Manganese	10 to 110 ng/m^3	1970-1974	Extensive	No recent (>1980) sampling data available
Methyl Bromide	Up to 1300 ppt	1982-1984	Extensive	Means of 5 - 250 ppt reported for various urban areas; most readings in ARB network in South Coast Air Basin < detection limit of 200 ppt
Mercury	Up to 50 ng/m^3	1968-1986	Limited	High values near sources; urban levels are 3 - 4 ng/m^3.
Nitrobenzenes	No data	-	None	Means up to 0.37 ppb and maximum of 2.8 ppb measured outside CA, 1977-1978
Nitrosomorpholine	No data	-	None	Up to 500 ppt in new car interiors

Table 29.2-2 (Continued)

SUMMARY OF AMBIENT GAS-PHASE CONCENTRATION DATA FOR CALIFORNIA

Level 2 Compound	California Concentrations	Dates	Size of Data Base	Comments
Phenol	Up to 87 ppb	1979	One set	Measured near point source; mean 17 ppb; urban means outside CA are 0.1 - 0.55 ppb phenol and 0.004 ppb 2-nitrophenol
Phosgene	Up to 61 ppt	1976	Limited	Means 16.5 - 40 ppt in 3 urban, 1 rural location
Propylene Oxide	No data	-	None	
Vinylidene Chloride	Up to 24.4 ppt	1981-1984	Limited	ARB monitoring network in South Coast Air Basin finds no values above detection limit of 100 ppt
Xylenes	Up to 45 ppb	1968-1984	Extensive[a]	Most CA urban values 3 - 20 ppb; no data for northern CA

[a] Data are extensive for southern California only.

Table 29.2-3

FIRST-STEP RANKING OF LEVEL 2 TOXIC AIR CONTAMINANTS

Ranked Rating Factors[a]			
E	UE.	UA	Compounds Meeting Rating Criteria
High	High	High	Acrolein
High	High	Medium	Monochlorobenzene, chlorobenzenes
High	High	Low	Acetaldehyde
High	Medium	High	Glycol ethers
High	Medium	Medium	
High	Medium	Low	Methyl bromide, xylenes
High	Low	High	
High	Low	Medium	
High	Low	Low	
Medium	High	High	Cresols
Medium	High	Medium	
Medium	High	Low	
Medium	Medium	High	1,4-dioxane, phenols, propylene oxide
Medium	Medium	Medium	
Medium	Medium	Low	
Medium	Low	High	
Medium	Low	Medium	
Medium	Low	Low	
Low	High	High	Acrylonitrile, allyl chloride, benzyl chloride, epichlorohydrin, maleic anhydride, mercury, nitrobenzenes, nitrosomorpholine, phosgene
Low	High	Medium	Dialkyl nitrosamines, manganese
Low	High	Low	
Low	Medium	High	
Low	Medium	Medium	Vinylidene chloride
Low	Medium	Low	
Low	Low	High	Chloroprene, hexachlorocyclopentadiene
Low	Low	Medium	
Low	Low	Low	

[a] E = Emissions, UE = Uncertainty in emissions, UA = Uncertainty in ambient concentration data.

et al., 1985). Reasonably good emission data were obtained in the present study for methyl bromide, 1,4-dioxane, phenols, propylene oxide, and vinylidene chloride. Emissions estimates for the remaining compounds were judged to be highly uncertain. Uncertainties in ambient concentration were rated as follows:

High = Data entirely lacking; available for a limited number of cases and/or geographic locations; or possibly outdated by changes in emission sources

Medium = Considerable data available but contains discrepancies or wide variability among investigators

Low = Extensive, recent monitoring data for a variety of sites

Table 29.2-3 shows our assignment of the 25 Level 2 potential toxic air contaminants to the ranked combinations of criteria. At this point in the selection process, the compounds may be grouped into four categories for selection for Phase II:

Highest Priority

Acetaldehyde, acrolein, chlorobenzenes, glycol ethers, monochlorobenzene, methyl bromide, xylenes

Secondary Priority

Cresols, 1,4-dioxane, phenols, propylene oxide

Lower Priority

Acrylonitrile, allyl chloride, benzyl chloride, dialkyl nitrosamines, epichlorohydrin, maleic anhydride, manganese, mercury, nitrobenzenes, nitrosomorpholine, phosgene, vinylidene chloride

To Be Eliminated

- Chloroprene, hexachlorocyclopentadiene

29.3 RANKING BY ATMOSPHERIC PERSISTENCE

From the data in Table 3.3-7, it is possible to rank the Level 2 compounds with respect to their atmospheric persistence. The most reactive compounds are the nitrosamines (dimethyl, diethyl, methylethyl, and nitrosomorpholine), which are removed by photolysis within 1 - 2 hours. Photolysis does not constitute a major removal process for other Level 2 compounds, whose atmospheric persistence is controlled by their reaction with OH. Figure 29.3-1 shows atmospheric residence times for a "typical" OH concentration of 10^6 molecules cm^{-3}. The residence times are calculated from $t_{1/2} = 0.69/k_{OH}(OH)$, where k_{OH} are either measured rate constants from the literature (dark circles in Figure 29.3-1) or rate constants calculated from structure-reactivity relationships (SRRs) (open circles in Figure 29.3-1).

The clustering of data in Figure 29.3-1 suggests that the Level 2 compounds can be divided into four reactivity groups. The first group, with half-lives of approximately 2 - 20 hours, includes hexachlorocyclopentadiene, chloroprene, the cresols, maleic anhydride, vinylidene chloride, 1,4-dioxane, acrolein, phenol, the xylenes, allyl chloride, acetaldehyde and the glycol ethers. The second group, with atmospheric half-lives of several days, includes acrylonitrile, epichlorohydrin, propylene oxide, the chlorobenzenes and benzyl chloride. The third group, with half-lives of several weeks, include the nitrophenols and nitrocresols. The last group, with half-lives of more than 100 days, includes nitrobenzene, methyl bromide, dinitrocresol, and phosgene. Reaction with OH is not a significant removal process for these compounds.

Several Level 2 compounds in the most reactive group with respect to reaction with OH also react with ozone. For a typical ozone concentration of 0.1 ppm (2.4×10^{12} molecules cm^{-3}), a compound with a reaction rate constant of 10^{-19} cm^3 $molecule^{-1}$ sec^{-1} will have a half-life of approximately one

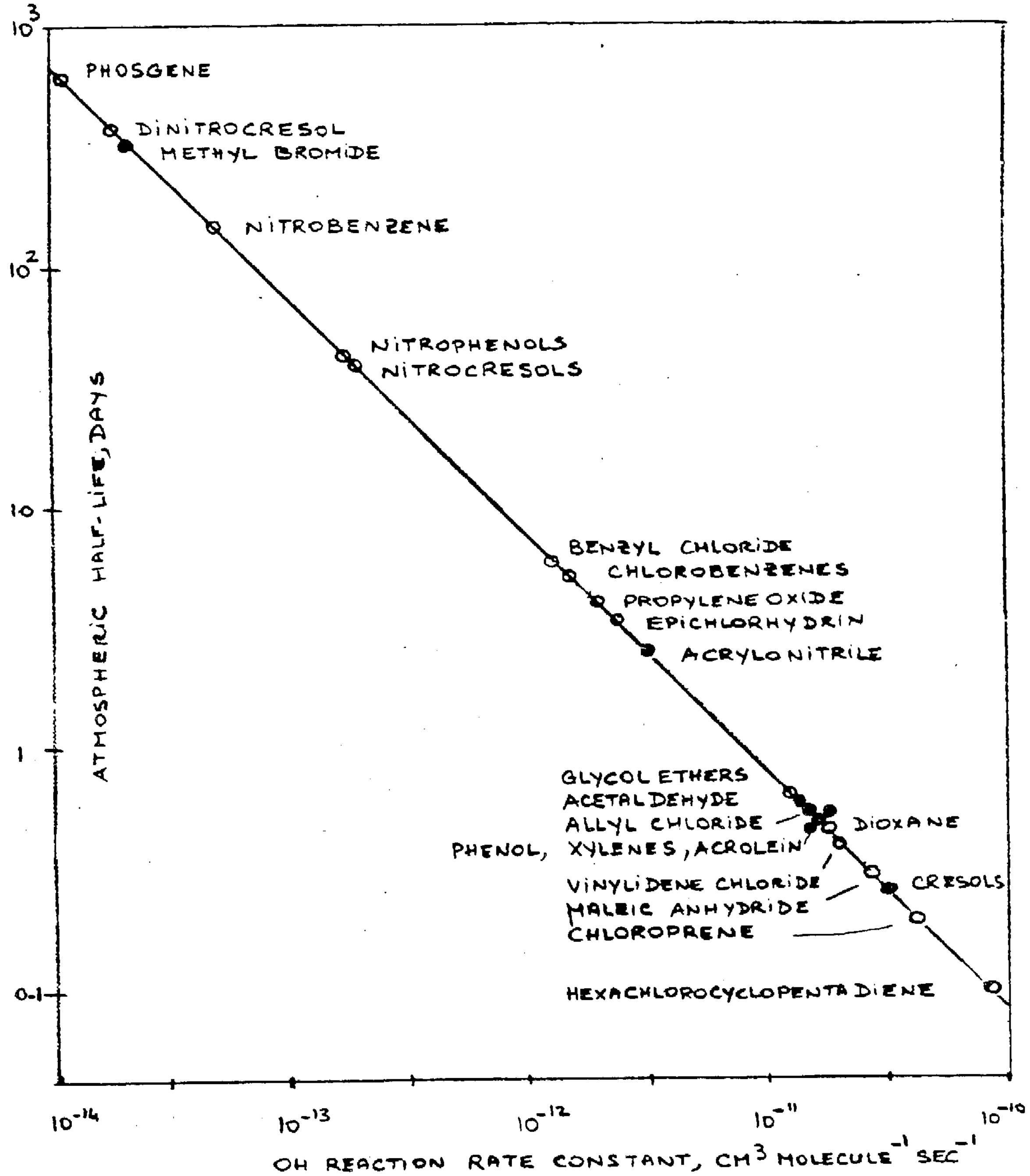

Figure 29.3-1. Atmospheric Removal of Level 2 Compounds by Reaction with OH for OH = 10^6 molecules cm^{-3}. Dark Circles are Measured OH Reaction Rate Constants. Open Circles are Rate Constants Estimated from SRR.

month (33.3 days). Using this value as a "cut-off" below which reaction with ozone is of negligible importance leaves only six Level 2 compounds: acrylonitrile, acrolein, allyl chloride, maleic anhydride, chloroprene and hexachlorocyclopentadiene (Table 29.3-1). For acrylonitrile, acrolein and allyl chloride, removal by reaction with OH dominates over that by reaction with O_3. The two processes are equally rapid ($t_{1/2} < 1$ day) for maleic anhydride, chloroprene, and hexachlorocyclopentadiene.

The last removal process for Level 2 compounds involves their reaction with NO_3 at night. For NO_3 = 50 ppt (1.2×10^9 molecules cm^{-3}), a compound with a reaction rate constant of 5×10^{-16} cm^3 $molecule^{-1}$ sec^{-1} will have a half-life of approximately one month (33.5 days). Using this value as a cut-off below which reaction with NO_3 is unimportant leaves 10 Level 2 compounds, plus probably the nitrophenols, for which no SRR estimate could be made. These compounds are listed in Table 29.3-2, along with their half-lives. Among the most reactive compounds are those which also react rapidly with OH and ozone, i.e. hexachlorocyclopentadiene, chloroprene and maleic anhydride. Level 2 compounds that are rapidly removed by NO_3, but not by ozone, are phenol, the cresols and probably the nitrophenols. Less reactive towards NO_3 are acetaldehyde and vinylidene chloride. Nighttime removal of these two compounds will only be appreciable at high NO_3 concentrations, e.g. approximately 1 ppb.

Table 29.3-3 lists the Level 2 potential toxic air contaminants which have been observed in the ambient air of California, and summarizes information on their atmospheric persistence and degradation products. On the basis of this information, we "promoted" cresols, dialkyl nitrosamines, phenols, and phosgene to the high-priority list. Vinylidene chloride was not promoted however, since it has low persistence in the atmosphere and is not a major precursor for ambient phosgene.

29.4 COMPOUNDS RECOMMENDED FOR PHASE II

On the basis of the three-step ranking exercise described in Sections 29.2 and 29.3, we recommend that the following 11 Level 2 compounds

Table 29.3-1

REMOVAL OF LEVEL 2 COMPOUNDS BY REACTION WITH OZONE

Reaction Rate Constant ($cm^3 molecule^{-1} sec^{-1}$)	Atmospheric half-life (days) for O_3 = 0.1 ppm	Level 2 Compound
10^{-16}	0.033 (approximately 50 minutes)	Hexachlorocyclopentadiene, Chloroprene
10^{-17}	0.33 (8 hours)	Maleic Anhydride
10^{-18}	3.33	Acrolein, Allyl Chloride
10^{-19}	33.3 (approximately one month)	Acrylonitrile
$<10^{-19}$	> 1 month	All other Level 2 Compounds

Table 29.3-2

REMOVAL OF LEVEL 2 COMPOUNDS BY REACTION WITH NO_3

Reaction Rate Constant ($cm^3 molecule^{-1} sec^{-1}$)	Atmospheric half-life (days) for NO_3 = 50 ppt	Level 2 Compound
10^{-12}	0.0067 (approximately 10 minutes)	Cresols (o,m,p), Phenol, Hexachlorocyclopentadiene
10^{-13}	0.067 (1.6 hour)	Chloroprene
10^{-14}	0.67 (16 hours)	Maleic Anhydride
10^{-15}	6.7	Acetaldehyde, Vinylidene Chloride
5×10^{-16}	33.5 (one month)	-
$< 5 \times 10^{-16}$	> 5 (months)	All other Level 2 Compounds

Table 29.3-3
COMPOUNDS CONSIDERED ON THE BASIS OF THEIR PRESENCE IN CALIFORNIA AMBIENT AIR

Compound	Atmospheric Persistence	Decision	Rationale
Acetaldehyde	Low	Yes	Already a high-priority compound
Acrolein	Low	Yes	Already a high-priority compound
Monochlorobenzene	Medium	Yes	Already a high-priority compound
Cresols	Low	Yes	Significant atmospheric formation; toxic secondary reaction products (PAN, HNO_3); more data on atmospheric chemistry are needed
Chlorobenzenes	Medium	Yes	Already a high-priority compound
Dialkyl Nitrosamines	Very low	Yes	Reaction products are highly toxic
Methyl Bromide	Very high	Yes	Already a high-priority compound
Phenols	Low	Yes	Net atmospheric production of nitrophenols and nitrocresols
Phosgene	Very high	Yes	Very persistent, toxic itself, product of many reactions
Vinylidene Chloride	Low	No	Low public exposure; only a minor source of atmospheric phosgene
Xylenes	Low	Yes	Already a high-priority compound

and compound groups be investigated further in Phase II:

- Acetaldehyde
- Acrolein
- Monochlorobenzene
- Cresols
- Chlorobenzenes
- Dialkyl nitrosamines
- Glycol ethers
- Methyl bromide
- Phenols
- Phosgene
- Xylenes

If resources permit, then the following compounds should be included in Phase II:

- 1,4-Dioxane
- Propylene oxide

Compounds which probably do not require further investigation as potential toxic air contaminants in California include:

- Acrylonitrile
- Allyl chloride
- Benzyl chloride
- Epichlorohydrin
- Maleic anhydride
- Manganese
- Mercury
- Nitrobenzenes
- Nitrosomorpholine
- Vinylidene chloride

Finally, the following compounds definitely do not require further investigation:

- Chloroprene
- Hexachlorocyclopentadiene

A plan for further investigation of the highest-priority compounds is presented in Chapter 31.

29.5 REFERENCES

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30.0

REVIEW OF SAMPLING AND ANALYTICAL TECHNIQUES FOR LEVEL 2 POTENTIAL TOXIC AIR CONTAMINANTS RECOMMENDED FOR PHASE II

30.1 INTRODUCTION

Ambient air sampling and analytical techniques for the Level 2 potential toxic air contaminants recommended for Phase II are presented in this section. These compounds and compound classes include:

- Acetaldehyde
- Acrolein
- Chlorobenzenes
- Cresols
- Glycol ethers
- Methyl bromide
- Dialkyl nitrosamines
- Phenols
- Phosgene
- Xylenes

The information presented here is primarily from a recent ARB-sponsored literature review of analytical methods for ambient air monitoring and source testing for toxic organic compounds (James et al., 1986). Table 30.1-1 summarizes the sampling and analytical techniques that will be discussed here. Method detection limits and the typical air sample volumes required to attain those limits are included in the table.

30.2 ALDEHYDES -- ACETALDEHYDE AND ACROLEIN

Numerous methods have been developed for the determination of aldehydes in ambient air. The most appropriate method, which is applicable to both acetaldehyde and acrolein, is the DNPH/HPLC method. This method is selective, essentially free of interferences, and sensitive enough to be used for ambient air determinations. Two noteworthy versions of the sampling part of this method have been developed, one involving impinger sampling and the other utilizing solid sorbent samplers. In both cases, each carbonyl compound in the sampled air reacts with 2,4-dinitrophenylhydrazine (DNPH) to form an unique hydrazone derivative which can be determined by high-performance liquid chromatography (HPLC). The impinger version requires an acidified aqueous DNPH/isooctane mixture as the collection medium. The aqueous phase is later extracted with organic solvent, and this extract is

Table 30.1-1

SAMPLING AND ANALYTICAL METHODS FOR MEASURING HIGHEST-PRIORITY LEVEL 2 COMPOUNDS AND COMPOUND CLASSES IN AMBIENT AIR

Compound	Sampling/Analysis Method	Minimum Detectable Concentration ($\mu g/m^3$)	Typical Sampling Volume (Liters)
Acetaldehyde	DNPH-impinger collection/HPLC DNPH-SepPak C18 collection/HPLC	<2 - <5 <2	30 - 60 100
Acrolein	DNPH-impinger collection/HPLC DNPH-SepPak C18 collection/HPLC	NA[a] <0.7[b]	NA[a] 100
Chlorobenzenes	Tenax-GC collection/GC/MS	0.01 - 0.05	100
Cresols	Tenax-GC collection/GC/MS	NA	NA
Glycol Ethers	Charcoal Tube collection/GC/MS	200 - 500	NA
Methyl Bromide	CMS collection/GC/MS	0.0 - 0.8	25
Phenols	Tenax-GC collection/GC/MS	NA	NA
Phosgene	GC/ECD[c]	4[d]	NA
Secondary and Tertiary Amines	Silica Gel collection/GC/MS	NA	NA
TCE/PERC	CMS collection/GC/MS	0.01 - 0.2	100
Xylenes	Tenax-GC collection/GC/MS	0.008 - 0.04	130

[a] NA = Not available.

[b] Estimated value.

[c] Information on sampling methods was unavailable in cited references.

[d] Detection limit without preconcentration.

combined with the isooctane layer from the impinger. The combined extract/isooctane solution is concentrated and analyzed by HPLC with UV detection. For the solid sorbent method, air is sampled through a SepPak C18 cartridge impregnated with DNPH and phosphoric acid. The DNPH derivatives are recovered from the cartridge by elution with acetonitrile. The eluate is then analyzed by HPLC with UV detection.

30.3 CHLOROBENZENES

Of the available sampling methods, solid sorbents are probably the most effective and easiest to use for monochlorobenzene and other chlorobenzenes. The most commonly used sorbent, and the one utilized in EPA Method T01 (Riggin, 1984), is Tenax-GC. Air is sampled through a tube containing Tenax-GC, and after sampling the adsorbed compounds are thermally desorbed from the trap and into a gas chromatograph/mass spectrometer (GC/MS) for analysis. GC/electron capture detection (GC/ECD) or GC/Hall electrolytic conductivity detection (GC/HECD) can also be used for chlorobenzene analysis, and lower detection limits can be achieved using either of these two analysis methods. However, these two methods are more subject to sample matrix interferences than is the highly specific GC/MS method.

30.4 CRESOLS AND PHENOL

The most appropriate sampling method for cresols and phenol is Tenax-GC sorbent tube sampling (EPA Method T01). The method is identical to that used for chlorobenzene, and analysis is best performed using GC/MS. GC/flame ionization detection (GC/FID) or GC/photoionization detection (GC/PID) can also be used for the analysis of phenol and cresols, and one can attain lower detection limits with GC/PID. However, these two detection techniques are more prone to sample matrix interferences than GC/MS.

30.5 GLYCOL ETHERS

Of the various sampling methods that have been used for glycol ethers, the most appropriate involves collection on charcoal tubes. After collection the charcoal is desorbed with solvent, which is then analyzed using packed column GC/FID. GC/MS would be a more suitable analytical technique due to its high specificity.

30.6 METHYL BROMIDE

The method which appears most applicable for ambient air sampling for methyl bromide uses the solid sorbent carbon molecular sieve (CMS) as the sampling medium (EPA Method T02). During sampling, air is passed through a tube containing CMS, which traps the methyl bromide. For analysis, the CMS tube is thermally desorbed, and the methyl bromide is quantitatively transferred into either a GC/FID or GC/MS for detection and quantitation. GC/MS is the preferred method of analysis because of its high specificity.

30.7 DIALKYL NITROSAMINES

In the case of nitrosamines, which are formed by the interaction of amines and nitrogen oxides, we will be primarily concerned with measuring the secondary and tertiary amine precursor compounds. Few methods are available for the determination of secondary and tertiary amines. The most appropriate sampling method (NIOSH Method P&CAM 221) uses solid sorbent sampling (NIOSH, 1977). However, this method has not been used, or originally designed for, sampling ambient air. During sampling, air is passed through a tube containing silica gel, which traps the amines. The silica gel is subsequently desorbed with dilute sulfuric acid, which is neutralized with dilute base prior to analysis. Analysis is best performed by GC/MS.

30.8 PHOSGENE

The references reviewed for this chapter did not identify any methods for sampling phosgene in ambient air. Since the limit of detection of the recommended analytical method (GC/ECD) is rather high (4 $\mu g/m^3$), preconcentration of the air sample would be necessary. Therefore, some methods development may be necessary in Phase II.

For phosgene we will also be concerned with measuring the precursor compounds trichloroethylene (TCE) and tetrachloroethylene (PERC). These two compounds are best determined using methodology identical to that used for methyl bromide (EPA Method TO2). Air is sampled using CMS sorbent tubes followed by thermal desorption and GC/MS analysis. GC/ECD or GC/HECD can also be used for detection and quantitation, but these methods are more subject to sample matrix interferences than is the GC/MS method.

30.9 XYLENES

Sampling and analysis methods for xylenes are similar to those described for chlorobenzene. EPA Method TO1, which utilizes solid sorbent sampling, is the most appropriate sampling method. Air is sampled through tubes containing Tenax-GC sorbent followed by thermal desorption and GC/MS analysis. As with cresols and phenol, other analytical methods are available, but they are not as specific as GC/MS and are more prone to sample matrix interferences.

30.10 REFERENCES

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31.0

PHASE II RESEARCH PLAN

The purpose of Phase II of the evaluation of potential toxic air contaminants will be to correct, wherever possible, the data deficiencies identified in Phase I. In this chapter, we outline a program of field sampling, laboratory experimentation, modeling, and other activities for obtaining the information necessary to prioritize the remaining Level 2 potential toxic air contaminants for health risk assessment. Section 31.1 contains, on a compound-by-compound basis, recommended approaches for obtaining improved emissions data, including site visits, source testing, and surveys. Approaches for expanding the data base on ambient concentrations and for estimating population exposures are described in Section 31.2. Finally, a program of laboratory experimentation to improve our understanding of atmospheric formation and removal processes is presented in Section 31.3.

31.1 EMISSIONS CHARACTERIZATION

31.1.1 Acetaldehyde and Acrolein

Most of the acetaldehyde and acrolein emissions in the State are from mobile sources (chiefly automobiles and trucks), oil refineries, natural gas and distillate oil combustion, and industrial and residential wood combustion. Uncertainties in the emission factors used in Phase I were enumerated in Section 4.3.1.2 of Chapter 4. We recommend that, as part of the upcoming ARB program, "Measurement of Selected Toxic Substances from Gasoline-Powered Light-Duty Motor Vehicles," acetaldehyde be added to the compounds to be investigated (acrolein is already included), and that improved emission factors be developed.

The emission factors for refineries and for industrial and residential fuel use are based upon very limited source testing data and rough assumptions regarding the fractions of total aldehydes represented by acetaldehyde and acrolein. We therefore recommend that source tests be conducted on representative combustion processes. Once new acetaldehyde and acrolein emission factors are developed, they should be applied to all relevant source classification codes and area source categories in the Emission Data System (EDS).

31.1.2 Monochlorobenzene and Other Chlorinated Benzenes

In Phase I we were able to develop a reasonably reliable emission estimate only for consumer use of para-dichlorobenzene (p-DCB). Many industrial uses for chlorinated benzenes were identified, however. To reduce this data gap, we recommend a combination of source testing, industrial surveys, and literature reviews.

The present estimate of p-DCB emissions from the one p-DCB processor in California, PPG Industries, Inc. in Irwindale, is based upon site visit data gathered in the late 1970s and may not be accurate. We therefore recommend source tests at the facility. Process emissions are believed to account for about 81 percent of the total, so the emphasis should be upon vents from distillation, crystallization, and fractionation processes.

Monochlorobenzene, ortho-dichlorobenzene (o-DCB) and 1,2,4-trichlorobenzene (1,2,4-TCB) are used directly as industrial process solvents and may be present in various formulations, such as pesticides. We recommend conducting a survey of potential users of these compounds, who would likely be manufacturers of adhesives, paints, polishes, waxes, pharmaceuticals, and perfumes. The survey should determine the extent to which monochlorobenzene, o-DCB and 1,2,4-TCB are used directly, incorporated into formulations, used as ingredients in formulations, recycled and disposed. Emissions from these uses could then be estimated by applying appropriate emission factors to the processes reported by the survey respondents. A similar survey of dye manufacturers should be conducted to determine use and emissions of 1,2,4-TCB and 1,3,5-TCB. California manufacturers of insecticides and herbicides for which di- and tri-chlorobenzenes are known or believed to be used as feedstocks should be surveyed. Finally, the extent of use of Lasso^{TM} (which contains monochlorobenzene) and Paracide (which is p-DCB) should be determined from contacts with manufacturers and review of California pesticide use reports.

31.1.3 Cresols

The Phase I estimate of cresol emissions is highly uncertain, since it was obtained by apportioning a national estimate to California on the basis of population. Nevertheless, since cresols are used in a variety of industries and in several consumer products, emissions could be significant. We therefore recommend an industrial survey of the type outlined in Section 31.1.2. As o-cresol and p-cresol are crystalline at normal ambient temperatures, and all the cresols are relatively nonvolatile (with an average relative evaporation rate of about 1), special attention should be paid to the potential for particulate, as well as evaporative, emissions.

In Phase I, one cresol manufacturer, PMC Specialties Group, Inc. (Santa Fe Springs); one large user, U.S. Department of Energy-Sandia National Laboratory (Livermore); and several smaller users were identified. We recommend source tests at the manufacturing plant, the Livermore facility, and at one or two small facilities. The purpose of the Santa Fe Springs tests would be to update the emission estimate presented in Chapter 11. The purpose of the tests at the user facilities would be to develop accurate emission factors, which could then be applied to the facilities in the aforementioned industrial survey.

Finally, more information is necessary on the cresol and cresylic acid content of disinfectants and cleaning compounds. In Phase I we obtained information on the cresol content of several of these compounds. However, in Phase II it may be necessary to purchase market research data to determine the relative use of the different formulations.

31.1.4 Dialkyl Nitrosamines

As was discussed in Chapter 13, use of dialkyl nitrosamines in California is likely to be negligible. However, these compounds may form in the atmosphere from secondary and tertiary amine precursors. In Phase II, therefore, the focus should be upon characterization of precursor emissions. The main sources to be investigated include feedlots, leather tanneries, and use of synthetic cutting fluids.

Amine emissions from feedlots can be sampled directly by use of a surface isolation flux chamber. Samples should be collected under various weather conditions to determine a range of flux rates. Emission factors having units of amine emissions per unit area per 1000 animals could then be calculated. The next step would be to obtain data on California feedlot areas, number of animals, and seasonal use patterns from the California Department of Food and Agriculture publication "California Livestock Statistics." Using the emission factors with these data, area source emissions could be determined.

Emission factors and/or speciation data for leather tanning processes do not appear to be available. It will thus be necessary to conduct source tests at a representative sample of the 30 leather tanning facilities in California; operating characteristics and potential emissions from the remainder can be determined through a survey.

The potential for emissions of amines and/or dialkyl nitrosamines from use of synthetic cutting fluids may be difficult to quantify in the field. We recommend that laboratory tests be conducted to determine evaporation rates of the compounds of interest under different conditions. Net use of cutting fluids would then be determined through a survey.

Once amine emissions have been quantified, stoichiometric relationships and laboratory data on relative yields of different products can be used to estimate maximum likely dialkyl nitrosamine formation in the atmosphere.

31.1.5 Glycol Ethers

As discussed in Chapter 16, a large proportion of glycol ethers results from the use of these compounds in paints and coatings. Recently, coatings formulators have decreased their use of ethylene glycol monoethyl and ethylene glycol monomethyl ethers. The first step in the Phase II emissions evaluation, therefore, should be to determine the magnitude of this trend. However, even if paints and coatings use were completely eliminated, other industrial solvent uses could still be fairly significant.

The upcoming ARB project, "Inventory of Solvent Use and Emissions From Degreasing and Non-Architectural Surface Coatings in the South Coast Air Basin" will include a survey of non-architectural surface coating solvent use by firms emitting less than 25 tons per year of any criteria pollutant in the South Coast Air Basin. Two major goals of that study are to estimate speciated emissions from these sources and to develop methods to extend the results to other air basins. The survey, while focusing on degreasing and coating processes, is also supposed to gather information on other solvent use at each facility. Phase II research on glycol ether emissions should therefore incorporate the results of the other program. However, it will still be necessary to estimate emissions from larger point sources and from other area source categories, such as printing and consumer product use. We therefore recommend a survey of the industries not covered elsewhere, along with an update of SAIC's previous research on solvent use in consumer products.

31.1.6 Methyl Bromide

Our Phase I estimate of methyl bromide emissions from both agricultural and non-agricultural applications is reasonably accurate, and probably accounts for most of the emissions of this compound in California. However, industrial surveys by the Bay Area and South Coast air quality management districts have identified several potentially significant point sources in urban areas. Since methyl bromide is long-lived in the atmosphere, we recommend that Phase II include both site inspections and ambient sampling around Niklor Chemical Company, Inc. in Long Beach and Stapleton Spence Packing in San Jose, whose emissions have been estimated to be 17 and 1.6 tons/yr, respectively. The purpose of the site inspections would be to verify the actual use of the compounds and whether emission controls have been installed and are operating properly.

Information on industrial use of methyl bromide outside the two major air basins was unavailable in Phase I. In Phase II, a survey of food processing facilities in other urban areas, especially in the agricultural regions, should be conducted to determine methyl bromide use and the extent and effectiveness of emission controls.

In Chapter 20, the Pacific Ocean was identified as a potentially significant source of methyl bromide emissions. We suggest a two-step approach to investigating this source in Phase II. First, preliminary marine air and water sampling should be conducted to verify the presence of elevated levels of methyl bromide. If they are found, then detailed flux measurements should be conducted off both the southern and central coasts, during at least two seasons.

31.1.7 Phenols

According to our Phase I research, automobiles are the most important source of phenol emissions in the State. However, our estimate of 222 tons per year is based upon secondary information sources, and the validity of the original data has been questioned. The upcoming ARB program, "Measurement of Selected Toxic Substances from Gasoline-Powered Light-Duty Motor Vehicles," will include development of emission factors for phenol. These factors should be used, in conjunction with vehicle mileage estimates, to improve the estimate of phenol emissions from mobile sources.

As reported in Chapter 24, the Bay Area Air Quality Management District has identified several facilities in its jurisdiction which use phenol. Most of these are electronics or computer manufacturing firms, and their combined emissions are estimated to be at least 17 tons per year. Given the large concentration of such firms in the Bay Area, this estimate needs to be improved. We recommend a detailed survey of phenol use, recycling, disposal, and emission controls. As will be discussed in Section 31.2, ambient sampling and modeling should focus on this area also. Source tests may be necessary in cases where mass balance information is insufficient.

31.1.8 Phosgene

We do not recommend any emissions characterization activities for phosgene in Phase II, since phosgene is neither produced nor used in California. Instead, the relationships between observed ambient concentrations of phosgene and its those of its precursors (chiefly chlorinated ethenes) should be examined more closely. Perhaps a predictive model which related changes in ambient phosgene levels to changes in precursor emissions could be developed.

31.1.9 Xylenes

In Chapter 28, we estimated that automobile exhaust emissions account for almost half of the total xylene emitted in the State. We therefore recommend that xylenes be added to the set of compounds to be investigated in "Measurement of Selected Toxic Substances from Gasoline-Powered Light-Duty Motor Vehicles." Refineries should be contacted to determine whether the fraction of xylene in gasoline will increase, as has been predicted; emission factors should be adjusted to reflect the trend, if any.

The other major source of xylene emissions is industrial use of xylene-containing paints, coatings and adhesives. As noted in Chapter 28, there is considerable discrepancy between emission estimates based upon surveys by the Bay Area and South Coast air quality management districts and those based upon apportionment of national xylene use data. This discrepancy can be resolved by a new survey, which emphasizes the need to report both direct use of xylene and use of xylene-containing formulations such as paints. In the South Coast Air Basin, this type of information will be obtained through the aforementioned survey of "small" sources, and could be extended to other air basins. An additional survey of a stratified sample of facilities presently in the Emission Data System and emitting more than 25 tons per year of criteria pollutants should also be conducted to determine the proportion of xylene in the throughput for various coatings and adhesives processes.

31.2 AMBIENT SAMPLING AND MODELING

The objectives of the ambient sampling and modeling to be conducted in Phase II include:

- Confirming the presence in California ambient air of compounds for which little or no data were found in Phase I;
- Determining whether a compound's ambient concentration varies diurnally and/or seasonally;
- Supporting, through upwind-downwind sampling, the estimation of emissions from a point source; and
- Obtaining a preliminary estimate of population exposures around major point sources.

31.2.1 Ambient Sampling

31.2.1.1 Areawide Sampling

Of the Level 2 potential toxic air contaminants recommended for Phase II, relatively abundant ambient concentration data are available only for acetaldehyde, methyl bromide, and the xylenes. No data were found for m-cresol, p-cresol, diethyl nitrosamine, methyl ethyl nitrosamine, glycol ethers, and the nitrophenols. For some of the remaining compounds, measurement data were limited to a single geographic area, or to one day of sampling. Furthermore, all of the compounds for which ambient concentration data are deficient are emitted by a variety of sources dispersed throughout the urban areas of the State. Therefore, we recommend that an areawide sampling program be conducted for:

- Acrolein
- Monochlorobenzene
- o-Dichlorobenzene
- p-Dichlorobenzene
- 1,2,4-Trichlorobenzene
- 1,3,5-Trichlorobenzene
- o-, m- and p-Cresol
- Dimethyl nitrosamine

- Diethyl nitrosamine
- Methyl ethyl nitrosamine
- Ethylene glycol monoethyl ether
- Ethylene glycol monomethyl ether
- Ethylene glycol monobutyl ether
- Phenols
- Phosgene

Methods for collecting and analyzing ambient samples of these compounds were discussed in Chapter 30. We recommend collection of hourly, diurnal, and 24-hour samples at at least three locations in each of the major air basins, during at least two seasons. The sampling locations should be away from major point sources, and should be representative of public exposure.

31.2.1.2 Special Ambient Sampling

In addition to the areawide sampling, we recommend that the following special sampling programs be conducted:

- Urban "street canyon" sampling of Level 2 potential toxic air contaminants which are believed to be present in automobile and truck exhaust, including acetaldehyde, acrolein, dialkyl nitrosamines, phenols, and xylenes; and
- Sampling around known point sources of chlorobenzenes, cresols, methyl bromide, and phenols.

The purpose of the street canyon sampling would be to determine whether drivers and pedestrians are exposed to significantly higher levels of the compounds of interest than would be inferred from the results of the areawide sampling. The point source sampling would have two functions. First, results could be used in conjunction with modeling to "back-calculate" emission rates and therefore confirm emission estimates obtained through source testing or mass balance calculations. We recommend this use only in situations where meteorological conditions are favorable and other sources of the compound of interest are absent. The other, and in our opinion more important, function of the point-source sampling would be to ascertain whether population exposure in the neighborhood of the source was significantly higher than elsewhere in the general area. This would require that (1) sampling be conducted simultaneously in "control" areas in the same air basin and (2) samples be collected over a long enough period for statistically valid inferences to be made.

31.2.2 Modeling

The purpose of the air pollution modeling to be conducted in Phase II should be to identify potential areas of high exposure of the population to Level 2 compounds. While the ambient sampling program described in Section 31.2.1 will also serve this purpose, it will not be practical to sample all potential high-exposure areas. Indeed, the modeling could be used, as it was in Phase I of "Sources and Concentrations of Chloroform Emissions in the South Coast Air Basin," to identify locations for ambient sampling. Two types of modeling, point-source and basin-wide, are recommended for Phase II.

31.2.2.1 Point Source Modeling

The first consists of estimating both short-term (i.e. 1-hour, 8-hour or 24-hour) and long-term (annual average) concentrations around selected point sources, in order to assess the potential for significant population exposure. For both the the short-term and long-term modeling, actual source characteristics, such as emission rate, stack height, and operating schedule, should be used. For the short-term modeling, we recommend using the Industrial Source Complex Short-Term (ISCST) model, along with "worst-case" meteorology, to calculate the magnitude and location of maximum concentrations in populated areas around the sources. ISCST can simulate the effects of both stack-tip and building downwash, and can simulate line and area sources within a facility. It may be used to calculate 1-, 2-, 3-, 4-, 6-, 8-, 12- and 24-hour average concentrations for receptors on a user-specified grid. For the long-term modeling, we recommend using the Climatological Dispersion Model (CDM), a U.S. Environmental Protection Agency guideline model. CDM requires meteorological data in the form of a joint frequency distribution (JFD) of wind speed, wind direction and atmospheric stability. These data are readily available from the National Climatic Center for the National Weather Service stations and several military stations in California. JFDs can also be generated from hourly meteorological data collected at ARB and air pollution control district monitoring stations. CDM also requires average emission rates and source characteristics, and can handle emissions from both point and area sources. Results are expressed as annual arithmetic means for receptors on a user-specified grid.

31.2.2.2 Basin-Wide Modeling

This type of modeling should be applied to selected Level 2 potential toxic air contaminants whose emission sources are widely distributed throughout an air basin. Rather than modeling actual sources, generic point and area emission sources should be defined and placed on a suitable grid. Annual average concentrations should be calculated using CDM and historical meteorology. Modeling results can be used to identify areas of high potential ambient concentrations.

31.3 LABORATORY STUDIES OF ATMOSPHERIC REACTIVITY

Phase II should include detailed investigations of the atmospheric persistence of selected Level 2 potential toxic air contaminants. Both atmospheric formation and atmospheric removal processes should be evaluated, using small Teflon outdoor chambers and experimental protocols similar to those now recommended by the U.S. Environmental Protection Agency for its studies of atmospheric toxic substances.

All of the Level 2 toxics selected for Phase II, except methyl bromide, will be included in the proposed laboratory studies. Methyl bromide has no atmospheric precursors and essentially no chemical removal processes in the atmosphere. The compounds to be included in Phase II are listed in Table 31.3-1 along with the corresponding formation and removal processes recommended for study. Specific studies to be carried out are described below. These studies are based on the atmospheric persistence ranking presented in detail in Chapter 3 as well as on the formation and removal

Table 31.3-1
RECOMMENDED LABORATORY STUDIES OF LEVEL 2 COMPOUNDS

Level 2 Compound	Atmospheric Formation	Atmospheric Removal
Acetaldehyde	Large, many HC precursors	Has been extensively studied
Acrolein	OH + diene (e.g. butadiene)	OH, O_3, fast; NO_3
Chlorobenzene	None	OH, slow
Glycol ethers	None	OH, rapid
Cresols (ortho, meta, para)	From toluene + OH; emphasis on isomer	OH, NO_3, rapid; emphasis on p-cresol and m-cresol
Phenol and nitrophenols	OH + benzene, slow; OH + phenol (nitrophenols), fast	OH, NO_3, slow (nitrophenols) to fast (phenol)
Xylenes	None	OH, fast
Phosgene	From selected chlorinated hydrocarbons	None
Methyl bromide[a]	None	None
Nitrosamines	From amines	Photolysis, fast

[a] No laboratory studies planned for this compound.

reactions discussed for each pollutant in Chapters 4 to 26.

31.3.1 Acetaldehyde

Formation

The atmospheric precursors of acetaldehyde are too numerous for laboratory studies of acetaldehyde yields from each of these precursors. We recommend estimating acetaldehyde yields by computer kinetic modeling of the reactivity of a hydrocarbon mixture representative of morning Los Angeles air.

The initial hydrocarbon composition should be based on the latest field measurements, including those which took place in 1987 as part of the Southern California Air Quality Study (SCAQS). The multi-hydrocarbon model employed should be that recently developed at the California Institute of Technology, and adapted for use for computer simulations of smog chamber experiments. Knowing acetaldehyde yields for each hydrocarbon (~ 25 paraffins, 10 aromatics and 10 olefins) and the emission rates for these hydrocarbons (from the latest Air Resources Board emission inventory) will allow calculation of the amount of acetaldehyde formed in the atmosphere by *in-situ* reactions.

Removal

Removal processes have been extensively studied and these studies do not need to be repeated. A limited number of experiments should be carried out to confirm PAN yields from acetaldehydes-NO_x (OH chemistry, daytime) and acetaldehyde-NO_2-O_3 mixtures (NO_3 chemistry, nighttime).

31.3.2 Acrolein

Formation

One formation pathway, involving the reaction of OH with dienes (e.g. butadiene), should be studied, with focus on acrolein yields.

Removal

Rapid removal of acrolein is expected by reactions with OH and ozone. These reactions should be studied, with emphasis on the anticipated major reaction products (formaldehyde, glyoxal, formic acid, and glyoxylic acid).

31.3.3 Chlorobenzenes

Formation

Not applicable.

Removal

By slow reaction with OH; the expected products are chlorophenol, nitrochlorobenzene, chloroPAN and chlorinated dicarbonyls.

31.3.4 Glycol ethers

Formation

Not applicable.

Removal

By rapid reaction with OH. This reaction should be studied extensively for each of the glycol ethers, with emphasis on the expected major products (hydroxycarbonyls, hydroxyacids, alkoxy compounds, and several acetates).

31.3.5 Cresols

Formation

The formation of cresols form toluene has been extensively studied.

Phase II work should be limited to measuring the isomer distribution (ortho, meta and para cresol) in a few toluene-NO_x irradiation experiments.

Removal

The rapid removal of cresols by reactions with OH and with NO_3 has already been investigated for one isomer, ortho-cresol. Phase II should focus on para-cresol and meta-cresol and their reactions with OH and NO_3. Expected products are nitrocresols, aliphatic ketoacids, and PAN.

31.3.6 Phenol and Nitrophenols

Formation

In-situ formation of phenol and nitrophenols in the atmosphere involves the reaction of OH with benzene and phenol, respectively. Product yields should be determined for each precursor.

Removal

As for cresols, reactions with OH and with NO_3 are expected to be major removal processes. There is obvious overlap between formation and removal of phenols, cresols and the corresponding nitrophenols, i.e. phenol forms from benzene and leads to nitrophenols in competing pathways. Experiments should thus be designed to obtain simultaneously information on both formation and removal for phenolic compounds.

31.3.7 Xylenes

Formation

Not applicable.

Removal

The reaction of xylenes with OH has been studied previously, and a computer kinetic model describing the atmospheric chemistry of meta-xylene is being developed at the California Institute of Technology. Phase II studies should be limited to experiments on product yields from the other two isomers. Expected reaction products include dimethylphenols, nitrodimethyl phenols, and carbonyls.

31.3.8 Phosgene

Formation

Phosgene yields are needed for the major atmospheric precursors trichloroethylene, 1,1-dichloroethane, 1,1,1-trichloroethane, methylene chloride, tetrachloroethylene, and chloroform. Given the high toxicity of phosgene, handling of the compound should be limited to *in-situ* production of parts per billion (ppb) concentrations from the precursors of interest. If no suitable analytical method can be developed for these low levels of phosgene, phosgene production should be estimated by computer kinetic modeling of the OH-precursor reactions and the corresponding ARB emission inventory for the precursors.

Removal

Not applicable.

31.3.9 Experimental protocols

Laboratory studies of Level 2 toxic organics should be carried out using reactors constructed from FEP Teflon film. Teflon is the material of choice for this type of investigation, as it is transparent to sunlight, and thus allows for realistic photolysis and photooxidation experiments. Teflon film exhibits minimal susceptibility to contamination, and is chemically inert towards Level 2 compounds and their expected reaction products. Extensive studies carried out over the past ten years have led to a detailed knowledge of the advantages and limitations of Teflon film reactors used in "smog chamber" studies of atmospheric reaction pathways.

For each Level 2 compound studied, experiments to be carried out in 4 m^3 Teflon chambers should include the following sequence:

- A control run, with only the Level 2 compound in pure air in the dark. The Level 2 compound loss rate by diffusion to the reactor walls is determined from concentration vs time measurements.
- A photolysis run, involving sunlight irradiation of the Level 2 compound in pure air;
- An ozone reaction run, with mixtures of ozone and the Level 2 compound in pure air in the dark;
- A hydroxy radical run, with sunlight-irradiated mixtures of oxides of nitrogen and the Level 2 compound in pure air; and
- A nitrate radical run, involving mixtures of ozone, nitrogen dioxide, and the Level 2 compound in pure air in the dark.

All five experiments listed above need not be conducted for all compounds; only the dominant loss process(es) listed in Table 31.3-2 should be investigated. In addition, one or more "opportunity" run(s) may be scheduled to investigate, if warranted, specific aspects of the atmospheric chemistry of the Level 2 compound studied.

31.3.11 Analytical methods

A number of analytical methods will be required for the proposed laboratory studies of the atmospheric chemistry of Level 2 compounds. These methods can be divided into four categories (listed as A, E, T, and NA in Table 31.3-2):

- Methods currently readily available and requiring no further development, e.g. the DNPH method for acetaldehyde.
- Methods currently readily available for structural homologues but not for the Level 2 compound of interest. Simple tests will be needed to extend the applicability of these methods to the specific needs of this project, e.g. extension to para-cresol of existing gas chromatographic (GC) method for ortho-cresol.
- Methods not widely used but well documented in the scientific literature, e.g. chlorobenzene by photoionization GC. Some initial testing and calibration will be required.

Table 31.3-2

ANALYTICAL METHODS FOR LABORATORY STUDIES OF LEVEL 2 COMPOUNDS

Level 2 Compounds, Precursors, and Products	Method	Method Status[a]
Acetaldehyde	DNPH-liquid chromatography (LC)	A
PAN	Electron capture gas chromatography (EC-GC)	A
Acrolein	DNPH-LC	A
Butadiene	Photoionization GC	E
Formaldehyde	DNPH-LC	A
Glyoxal	DNPH-LC	A
Formic acid	Size exclusion ion chromatography (IC)	A
Glyoxylic acid	Size exclusion IC	A
Chlorobenzene	EC-GC	E
Chlorophenol	EC-GC or LC with UV detection	T
Nitrochlorobenzene	Same as chlorophenol	T
Chloro PAN	EC-GC	E
Chlorinated carbonyls	DNPH-LC	T
Glycol ethers	Liquid chromatography (LC)	T
Hydroxycarbonyls	DNPH-LC	T
Hydroxy acids	Size exclusion IC	T
Alkoxy products	LC, flame ionization GC	T
Acetates	Flame ionization GC	T
Cresols	Photoionization GC	E
Toluene	Photoionization GC	E
Nitrocresols	LC-UV	E
Aliphatic ketoacids	Size exclusion IC	A
PAN	EC-GC	A
Phenol	LC-UV	E
Nitrophenol	LC-UV	E
Nitrocresol	LC-UV	E
Dicarbonyls	DNPH-LC	A
Xylenes	Photoionization GC	E
Dimethylphenols	Flame ionization GC, photoionization GC, LC-UV	E
Nitrodimethylphenols	LC-UV	E

Table 31.3-2 (Continued)

ANALYTICAL METHODS FOR LABORATORY STUDIES OF LEVEL 2 COMPOUNDS

Level 2 Compounds, Precursors, and Products	Method	Method Status[a]
Dicarbonyls	DNPH-LC	A
Phosgene	No method currently available	NA
Trichloroethylene	EC-GC	A
1,1-dichloroethane	EC-GC	A
1,1,1-trichloroethane	EC-GC	A
Methylene chloride	EC-GC	A
Chloroform	EC-GC	A
Tetrachloroethylene	EC-GC	A

[a] A = method readily available and directly applicable to Level 2 compound.
E = method readily available and can be extended to include Level 2 compound.
T = method described in the literature; must be tested further.
NA = method not available; significant development effort required.

- Methods of general applicability but not yet tested for Level 2 compounds or their expected reaction products, e.g. measurements of nitrochlorophenol by GC. Substantial effort will be required to test and calibrate these new methods prior to their application to this project.