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EVALUATION OF POTENTIAL TOXIC AIR CONTAMINANTS
PHASE I

FINAL REPORT

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DISCLAIMER

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ABSTRACT

As part of the toxic air contaminant regulatory process required by California Assembly Bill 1807 ("the Tanner Bill"), the California Air Resources Board (ARB) has divided candidate toxic compounds into two major classes. "Level 1" compounds are those for which sufficient information exists to initiate a full health effects evaluation. "Level 2" compounds are those which require additional documentation to determine whether further action under the Tanner Bill is necessary. Level 2 potential toxic air contaminants include acetaldehyde, acrolein, acrylonitrile, allyl chloride, benzyl chloride, chlorobenzene(s), chloroprene, cresols, p-dichlorobenzene, dialkyl nitrosamines, 1,4-dioxane, epichlorohydrin, glycol ethers, hexachlorocyclopentadiene, maleic anhydride, manganese, methyl bromide, mercury, nitrobenzenes, nitrosomorpholine, phenol(s), propylene oxide, vinylidene chloride, and xylenes.

The objectives of this study, which constitutes Phase I of a planned two-phased program, were to obtain information on the use, emissions, ambient concentrations, and atmospheric chemistry of the 25 Level 2 compounds and compound classes; to identify data deficiencies; to recommend compounds for further study in Phase II; and to outline a program of field measurement, surveys, modeling and laboratory experimentation to reduce the data gaps.

Research under this project began with compilation of dossiers on each of the 25 Level 2 potential toxic air contaminants. Preliminary information on direct and indirect production, industrial use and emissions, and consumer use of the compounds was obtained through a review of existing inventories, and surveys of chemical producers and industrial users. Statewide emissions were estimated for most of the compounds. Ambient concentration data were obtained by a literature review. Atmospheric formation and removal processes were postulated through a literature review and application of theoretical principles; where reaction rates were unavailable they were estimated on the basis of available data for structural homologues.

After the dossiers were completed the Level 2 potential toxic air contaminants were ranked on the basis of their estimated emissions, uncertainty in emission estimates and ambient concentration data, and stability in the atmosphere (including the potential for formation of toxic degradation products). Compounds highly recommended for Phase II investigation include acetaldehyde, acrolein, monochlorobenzene and other chlorinated benzenes, cresols, dialkyl nitrosamines, glycol ethers, methyl bromide, phenols, phosgene, and xylenes.

The recommended program for Phase II includes source tests at several facilities to improve emission estimates and/or develop new or improved emission factors; detailed surveys of selected industries; ambient sampling throughout the major air basins and in the vicinity of certain point sources; modeling of ambient concentrations near sources and in certain air basins; and smog chamber experiments to confirm theoretical predictions of atmospheric reaction products and rates.

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FINDINGS AND CONCLUSIONS

Complete dossiers on the 25 Level 2 potential toxic air contaminants are found in Chapters 4 through 28. Sections 1.1 through 1.3 of this chapter summarize, for each compound or compound group, California use and emissions, ambient concentrations, and atmospheric chemistry. In Section 1.4, our ranking of Level 2 potential toxic air contaminants for suitability for further research in Phase II is presented.

1.1 CALIFORNIA PRODUCTION, USE AND EMISSIONS

Table 1.1-1 summarizes the information obtained through this project on the types of sources of Level 2 potential toxic air contaminants, estimates of the statewide emissions of the compounds, and the uncertainties in the emission estimates. Atmospheric chemistry of these compounds is discussed in Section 1.3. Specific data on each Level 2 compound and compound group are as follows.

1.1.1 Acetaldehyde

(1) No acetaldehyde is produced or used as an industrial feedstock in California.

(2) Acetaldehyde is produced and emitted through a variety of combustion sources, including automobiles (1,400 - 2,500 tons/yr), trucks (1,800 - 4,800 tons/yr), aircraft (230 tons/yr), electric power plants (120 tons/yr), oil refining (1,200 tons/yr), industrial and residential fossil fuel use (1,300 tons/yr), wood combustion (1,700 tons/yr), tobacco smoke (36 tons/yr) and coffee roasting (0.1 - 1 ton/yr).

(3) Some acetaldehyde may be present in acetone and in other consumer products, but emissions from these sources are likely to be negligible when compared with indirect production.

(4) Statewide emissions are estimated to be 7,800 - 12,000 tons/yr. This figure is fairly uncertain, given the scarcity of data on emission factors for combustion sources.

Table 1.1-1

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.

1.1.2 Acrolein

(1) No acrolein is produced or used as an industrial feedstock in California.

(2) Acrolein is produced and emitted through a variety of combustion sources, including automobiles (270 - 760 tons/yr), trucks (585 - 2,370 tons/yr), aircraft (50 tons/yr), electric power plants (27 tons/yr), oil refining (260 tons/yr), industrial and residential fossil fuel use (290 tons/yr), wood combustion (300 tons/yr), tobacco smoke (50 tons/yr) and coffee roasting (0.1 - 1 ton/yr).

(3) Acrolein is not present in consumer products.

(4) Statewide emissions are estimated to be 1,800 - 4,100 tons/yr. This figure is fairly uncertain, given the scarcity of data on emission factors for combustion sources.

1.1.3 Acrylonitrile

No acrylonitrile is produced in California. According to inventories developed by the Bay Area and South Coast air quality management districts, about 2.8 tons per year are emitted from use of the compound to manufacture acrylonitrile-butadiene-styrene (ABS) and acrylic resins at about 30 facilities; however, information obtained in this project indicates that the statewide total may actually be as low as 0.4 ton. There are no consumer uses, and there is no evidence for a significant release of acrylonitrile from finished ABS and acrylic resins.

1.1.4 Allyl Chloride

No allyl chloride is produced in California. The only potential source of allyl chloride emissions in the state is from manufacture of phenol-formaldehyde resins at one location in Los Angeles County. Our emission estimate of less than 0.25 ton per year is highly uncertain.

1.1.5 Benzyl Chloride

Benzyl chloride is not produced in California. One out-of-state benzyl chloride manufacturer reported that it shipped the compound to a

California manufacturer of quaternary ammonium salts; this manufacturer could not be identified, however. Benzyl chloride is also used (in other states) to produce benzyl phthalate plasticizers for polyvinyl chloride (PVC) products. Outgassing of benzyl chloride trapped as a contaminant in PVC which contained butyl benzyl phthalate has been reported in the literature. Only one U.S. PVC manufacturer reported using benzyl phthalate plasticizers, however, so emissions from this source are likely to be negligible. Benzyl chloride is not used directly in any consumer products. An unknown, but probably negligible, amount of emissions may occur from release of benzyl chloride present as a contaminant in benzyl chloride derivatives used in these products.

1.1.6 Monochlorobenzene

No monochlorobenzene is produced in California. The compound has been identified in a variety of settings known to be present in California, although the locations and amounts of emissions cannot be determined from available data. Potential sources are as follows.

(1) About 1.7 tons per year of chlorobenzene are emitted by wastewater treatment plants in California.

(2) Chlorobenzene has numerous industrial uses, including the manufacture of adhesives, paints, polishes, waxes, resins, drugs, and perfumes. The extent of monochlorobenzene use in these applications in California is unknown.

(3) Chlorobenzene is a solvent/carrier in the herbicide Lasso™. Information on the monochlorobenzene content of Lasso formulations used in California is proprietary and cannot be reported.

(4) Other consumer uses are parts degreasing, solvent for gloss white butyrate lacquer, and solvent for certain types of adhesives. Again, it is not known to what extent products with monochlorobenzene are used in California.

1.1.7 Chloroprene

Chloroprene is only used captively in the manufacture of neoprene rubber outside California. It is highly unlikely to be present in California.

1.1.8 Cresols

PMC Specialties Group, Inc., the sole manufacturer of cresols and cresylic acids in California, was estimated to have emitted 17 tons of cresol in 1978; a more recent estimate cannot be reported without revealing proprietary data. The likely California industrial end uses for cresols and cresylic acids are manufacture of tri-cresylic phosphate and cresyl diphenol phosphate, production of phenolic resins, use as a solvent for wire hanger enamel, manufacture of pesticides, and use as an ore flotation agent. We estimate that over 714 tons of cresols are released to the atmosphere annually due to these industrial activities. Disinfectant/cleaning compounds are the major cresol-containing consumer products; others include metal degreasing agents, inks, and some paint removers. We estimate that approximately 137 tons/yr of cresols are emitted from consumer products. Total cresol emissions in the state are about 900 tons per year.

1.1.9 Chlorobenzenes

(1) None of the chlorobenzenes reviewed in this study, ortho-dichlorobenzene (o-DCB), para-dichlorobenzene (p-DCB), 1,2,4-trichlorobenzene (1,2,4-TRCB), and 1,3,5-trichlorobenzene (1,3,5-TRCB) is manufactured in California, although p-DCB is isolated at one plant from a crude mixture of dichlorobenzenes.

(2) There is limited evidence that p-DCB may form as a byproduct of carbon tetrachloride (CT) manufacturing; it could therefore be present in vent releases from a CT plant in Pittsburg. Chlorination of drinking water is not a significant source of chlorinated benzenes. Formation of chlorobenzenes during wastewater treatment has been reported in the literature, but has not been confirmed by recent studies. Various chlorobenzenes may also be products of metabolism and degradation of the insecticide lindane.

(3) The chlorobenzenes are used in a variety of industrial settings. We found no evidence that o-DCB is used in California as a feedstock for chloroaniline compounds or toluene diisocyanate. It is possible that it is used industrially as a coolant for magnetic coils, heat transfer medium, degreasing agent, and solvent, although the extent of this o-DCB use in the state is unknown. Para-dichlorobenzene is isolated from a mixture of dichlorobenzenes at a facility in Irwindale. A published, but highly uncertain, estimate of emissions from this facility is 3.85 tons per year. PDCB has several other industrial uses, including pesticide manufacturing, but none appears to be significant in California. The two trichlorobenzenes investigated are also used industrially as pesticide intermediates and solvents, but we could find no information on the extent of their use in California.

(4) Para-dichlorobenzene is a major constituent of moth control blocks and room deodorants. California emissions from these consumer products are estimated to be 3,000 tons per year. It is also used, to an unknown extent, as a direct pesticide and soil fumigant.

1.1.10 Dialkyl Nitrosamines

None of the three dialkyl nitrosamine compounds of interest, dimethyl nitrosamine (DMN), diethyl nitrosamine (DEN), and methylethyl nitrosamine, is produced in California. Nitrosamines may form in the atmosphere from reactions with secondary and tertiary amines. They have been found in some industrial processes, high explosives, livestock and poultry manure, animal rendering plants, and leather tanneries. Amine precursors are used in the preparation of rubber accelerators, pharmaceuticals, herbicides, fungicides, and insecticides, and in the leather tanning industry. DMN is used as an industrial solvent, antioxidant, solvent in the fiber and plastics industry, and in lubricants and condensers. DEN has been used as a gasoline and lubricant additive. Alkyl amines emitted by motor vehicles are unlikely to be significant precursors for dialkyl nitrosamines. The amounts of dialkyl nitrosamines emitted to the atmosphere and formed *in situ* are not presently known.

1.1.11 1,4-Dioxane

No 1,4-dioxane is produced, used as a feedstock, or released as a

byproduct of any manufacturing process in California. The main use of the compound is as a reaction inhibitor in methyl chloroform (1,1,1-trichloroethane). Although there is some discrepancy among different estimates of methyl chloroform use in the state, corresponding 1,4-dioxane emissions are probably between about 200 and 600 tons per year.

1.1.12 Epichlorohydrin

Epichlorohydrin is not produced deliberately in California. No facilities for its primary industrial use, manufacturing of epoxy resins and synthetic glycerin, are located in the state. Less than 0.1 ton/year of epichlorohydrin emissions occur from various other manufacturing uses in the San Francisco Bay and South Coast air basins. Consumer products containing epichlorohydrin include paints, varnishes, lacquers, nail enamels, and pesticides. Small amounts of the chemical may be trapped as a contaminant in epichlorohydrin elastomer products. It appears that the use of products which contain epichlorohydrin might be widespread; however, it is not presently possible to quantify the distribution of such products or their epichlorohydrin emissions.

1.1.13 Glycol Ethers

Glycol ethers are not produced in California. No indirect pathways to the formation of glycol ethers appear to exist either. A variety of industrial formulations, such as fuel additives, protective coatings, printing inks, and leather dyes, contain glycol ethers as solvents. Consumer products which may contain glycol ethers include gasoline, brake fluids, insecticides, detergents, cosmetics, adhesives, and liquid household cleaners. We estimate that direct industrial use accounts for over 4,950 tons/yr of ethylene glycol monobutyl ether, and over 5,750 tons/yr of ethylene glycol monoethyl ether. We also estimate that approximately 200 tons/yr of ethylene glycol monoethyl ether are released by direct industrial use, but we are unable to estimate industrial and consumer emissions from products which contain this compound. Annual California emissions of these three glycol ethers from industrial uses are approximately 11,000 - 12,450 tons/yr. Annual emissions from consumer products are 1,450 tons. Thus,

total California emissions of these glycol ethers is between 12,400 and 13,850 tons/yr.

1.1.14 Hexachlorocyclopentadiene

It is highly unlikely that hexachlorocyclopentadiene is emitted into the California ambient air. The only manufacturer neither produces the compound in California nor ships it into the state. The only industrial uses are as intermediates in the manufacturing of flame retardants and chlorinated hydrocarbon pesticides. It appears that this type of industrial activity does not take place in California.

1.1.15 Maleic Anhydride

Maleic anhydride is not produced in California. The only potential sources of maleic anhydride emissions in California are unsaturated polyester resin and alkyd resin manufacturing plants. Inventoried emissions from these facilities are about 8.0 tons (7.3 kkg) per year. This value is highly uncertain, given the lack of established emission factors.

1.1.16 Manganese

(1) Manganese is not produced in California.

(2) The primary industrial use of manganese is as an additive to strengthen and harden iron and steel products, although minor uses exist in copper, nickel, and aluminum alloys and in production of carbon-zinc dry cell batteries. We estimate that emissions from steel production are 0.18-5.9 tons/yr and those from cast iron production are about 0.02-0.52 ton/yr.

(3) Between 9 and 30 tons/yr of manganese are estimated to be emitted by automotive exhaust, due to the presence of manganese in gasoline. Use of methylcyclopentadienyl manganese tricarbonyl (MMT) as an octane booster contributes another 46 tons per year. Mn is being considered as an additive to diesel fuels to help purge and regenerate ceramic particulate trap filters in diesel engines.

(4) Assuming that all manganese present in fuel oil is emitted, we estimate that up to 0.09 ton/yr of Mn is emitted by residual fuel oil combustion in California. Coal combustion contributes another 1.0 to 1.6 tons/yr.

(5) A rough estimate of manganese emitted from sludge incineration in the state is 0.01 ton/yr.

(6) Manganese sulfate and manganous oxide are used in soil conditioners. The extent of production of airborne manganese from this source is not known. In addition, soil and road dust make an unknown contribution to ambient levels.

(7) Total statewide manganese emissions accounted for in this review are about 56 to 84 tons/yr.

1.1.17 Methyl Bromide

Methyl bromide is not manufactured in California. Potentially large amounts of the compound may be produced biologically in the ocean off the California coast, although this remains unconfirmed at present. No indirect production of methyl bromide takes place in the state. It is not known to what extent the chemical is used industrially as a methylating or wool degreasing agent or disinfectant. However, industrial emissions are likely to be minor compared to the 3,500 tons per year of methyl bromide which are released through use of the compound as a soil fumigant in California. Methyl bromide may also be released through its use in special purpose fire extinguishers.

1.1.18 Mercury

Estimates of elemental mercury emissions from all identified sources in California are quite uncertain. These emissions, however, are likely to be small. One California mine produces mercury in conjunction with gold. Emissions from associated ore processing are about 0.12 ton/yr. The main indirect sources of mercury include municipal sewage sludge incineration, geothermal power production, and fossil fuel combustion. Releases from these sources are estimated to be 0.07, 0.3 - 0.4, and 0.09 - 0.9 ton/yr, respectively, for a total of 0.4 - 1.4 tons/yr. A lower bound for industrial emissions, which occur from mainly from use of mercury in instrument manufacturing, electroplating and used battery reclamation, is about 0.24 ton/yr. Unknown amounts of mercury may be released from use of consumer products and from dental amalgams. It is unlikely that total emissions in the state exceed 2 tons/yr.

1.1.19 Nitrobenzene

Nitrobenzene is not directly produced in California, but may form in the atmosphere in the presence of benzene. Its industrial use in the state, chiefly in electronics manufacturing, is unknown but does not appear to be major. Consumers may be exposed to small amounts of nitrobenzene from a variety of products such as shoe polish, floor polish, metal polish, some soaps, perfume, and leather dressings.

1.1.20 Nitrosomorpholine

Nitrosomorpholine is not deliberately produced or used; it is believed to form in the atmosphere from the nighttime reaction of nitrous acid with morpholine. Morpholine is not produced in California. The main uses for the compound are as an ingredient in rubber accelerators, corrosion inhibitors, optical brighteners, waxes and polishes. The only significant sources of morpholine emissions in California are likely to be the use of corrosion inhibitors and waxes and polishes. No recent data on these uses were available. Using old and highly uncertain data, we estimate that a maximum of 1.1 MM lb of morpholine were released in California in 1978. If all of this were converted to nitrosomorpholine by atmospheric reaction, then production would be about 700 tons per year. Most of this atmospherically generated nitrosomorpholine would be rapidly removed by photolysis, and would not accumulate in the atmosphere during daytime.

Work settings where elevated concentrations of nitrosomorpholine could occur are rubber tire manufacturing and leather tanning. 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.

1.1.21 Phenols

(1) Emissions from the only phenol producing facility in California, which is in Santa Fe Springs, are approximately 1.2 tons/yr.

(2) Indirect sources of phenol emissions include automobile exhaust (about 222 tons/yr) and wood combustion (276 tons/yr). Emissions from volatilization from wastewater are probably negligible.

(3) The only industrial use of phenol in the state is the production of phenol-formaldehyde resins by at least 7 facilities. We estimate that 15 tons/yr of phenol are released from these sites.

(4) Total California phenol emissions are approximately 514 tons/yr.

1.1.22 Phosgene

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

1.1.23 Propylene Oxide

Propylene oxide (PO) is not produced in California. Statewide emissions of PO 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 available emission estimates are highly uncertain.

1.1.24 Vinylidene Chloride

The only likely sources of vinylidene chloride (VDC) 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. Emissions in the rest of the state are about 0.6 ton/yr, for a total of 3.8 - 4.1 tons/yr.

1.1.25 Xylenes

(1) No manufacturers of isolated mixed xylenes are located in California; we do not presently know whether non-isolated xylenes are produced in the state.

(2) No manufacturing plants in California use individual xylene isomers as feedstocks.

(3) Emissions from industrial formulation of xylene-containing products; use of paints, coatings and adhesives; and direct use of xylenes as solvents are about 14,900 tons/yr. This value exceeds considerably the combined total of estimates developed by the Bay Area and South Coast air quality management districts; however, these districts' inventories may have ignored emissions from use of xylene-containing industrial paints and coatings. In any event, industrial emissions are uncertain.

(4) Use of nonindustrial paints and coatings and other consumer products accounts for about 1,370 tons/yr of xylene emissions.

(5) Automotive-related uses, which include evaporation from automobiles, evaporation from gasoline marketing, and automotive exhaust gases, account for another 16,200 tons/yr.

(6) Total annual California xylene emissions are approximately 32,500 tons.

1.2 AMBIENT CONCENTRATIONS IN CALIFORNIA

One of the main objectives of this project was to obtain as much information as possible on ambient concentrations of the Level 2 potential toxic air contaminants in California, and to identify important data gaps. Table 1.2-1 summarizes the results of the review of ambient concentration data. Some of our principal findings are:

(1) No data were found on concentrations of acrylonitrile, allyl chloride, benzyl chloride, chloroprene, m-cresol, p-cresol, dialkyl nitrosamines other than dimethylnitrosamine, p-dichlorobenzene, trichlorobenzenes, 1,4-dioxane, epichlorohydrin, glycol ethers, hexachlorocyclopentadiene, maleic anhydride, nitrobenzenes, nitrosomorpholine, or propylene oxide in the ambient air of California.

(2) An extensive California ambient air data base exists for acetaldehyde, methyl bromide, and xylenes.

Table 1.2-1

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 1.2-1 (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 1.2-1 (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.

(3) Limited information, generally from fewer than 10 sets of sampling data, was available for acrolein, monochlorobenzene, o-cresol, o-dichlorobenzene, m-dichlorobenzene, dimethylnitrosamine, mercury, phenol, phosgene, and vinylidene chloride.

(4) Reported concentrations of acetaldehyde, acrolein, monochlorobenzene, cresols, phenol, and xylenes are generally in the range of 20 to a few hundred parts per billion (ppb). Dichlorobenzenes, dialkyl nitrosamines, methyl bromide, phosgene and vinylidene chloride, in contrast, are present in the range of about 10 to several hundred parts per trillion (ppt).

(5) The geographical coverage of the existing ambient data is quite limited; the great majority of reported California measurements were made in the South Coast Air Basin.

(6) The data for acrolein, dimethylnitrosamine, and phosgene were collected before 1978 and may be different if measured today, given changes in the nature and strengths of many sources of precursors to atmospheric formation of these compounds.

(7) Ambient data reported for o-cresol, o-dichlorobenzene, m-dichlorobenzene, mercury, and phenol were obtained near point sources of these compounds. General ambient levels of these compounds are expected to be much lower, i.e. 1 ppb or less.

1.3 ATMOSPHERIC CHEMISTRY

1.3.1 In-Situ Formation of Level 2 Compounds

Table 1.3-1 shows which of the Level 2 potential toxic air contaminants are likely to form in the atmosphere, and identifies their precursors. The findings of our investigation of in-situ formation processes may be summarized as follows.

(1) In-situ formation, through reaction of the hydroxyl radical (OH) with chloroethenes and chloromethanes, is probably the only source of ambient phosgene in California.

(2) Atmospheric reactions are probably responsible for a significant fraction of the acetaldehyde and cresols observed in the atmosphere in the South Coast Air Basin and, perhaps, in other urban areas of California.

(3) Theoretical considerations and laboratory evidence suggest that acrolein, monochlorobenzene and other chlorobenzenes,

Table 1.3-1

IN-SITU FORMATION OF LEVEL 2 POTENTIAL TOXIC AIR CONTAMINANTS

	Atmospheric Reaction Precursors	Importance of In-Situ Formation
Acetaldehyde	O_3, OH and all methyl paraffins; OH + some paraffins; aromatics; cresols; propylene oxide	Major (50-200 tons/day in SCAB)
Acrolein	OH, O_3 + dienes (e.g. butadiene)	Unknown
Acrylonitrile	None	-
Allyl Chloride	None	-
Benzyl Chloride	None	-
Monochlorobenzene	Benzene, Cl (only near source)	Unknown
Chloroprene	None	None
Cresols	OH + toluene	Major (3,650-16,790 tons/yr)
Chlorobenzenes	Benzene, Cl (only near source)	Unknown
Dialkyl Nitrosamines	HONO + amines (dark) OH + amines (daytime)	Unknown Unknown
1,4-Dioxane	None	None
Epichlorohydrin	None[a]	None
Glycol Ethers	None	None
Hexachlorocyclopentadiene	None	None
Maleic Anhydride	OH + benzene, toluene, o-xylene[b]	
Manganese	None	None
Methyl Bromide	None	None
Mercury	Dimethyl mercury (daytime)	Unknown
Nitrobenzenes	OH + benzene	Important?
Nitrosomorpholine	Morpholine + HO, NO_x	Unknown
Phenols	OH + Benzene	Unknown
Phosgene	Halocarbons[c]	Only source
Propylene Oxide	None[d]	None
Vinylidene Chloride	None	None
Xylenes	None	None

[a]Epichlorohydrin may form by reaction of atomic oxygen with allyl chloride, but this reaction is not expected to be important in ambient air.

[b]Formation of maleic anhydride from these precursors may occur, but has not been fully documented.

[c]Precursors, in decreasing order of importance, are trichloroethylene, 1,1-dichloroethane, 1,1,1-trichloroethane, methylene chloride, tetrachloroethylene (perchloroethylene), and chloroform.

[d]Propylene oxide may form by reaction of atomic oxygen with propene, but this reaction is not expected to be important in ambient air.

dialkyl nitrosamines, maleic anhydride, elemental mercury, nitrobenzenes, nitrosomorpholine, and phenol may form in the atmosphere; however, ambient concentration data are insufficient to determine the existence and importance of these reactions.

(4) It is interesting to note that some Level 1 toxic air contaminants (benzene, chloroform, methylene chloride, 1,1,1-trichloroethane, trichloroethylene, and tetrachloroethene) are precursors for Level 2 compounds; control of the former could therefore result in reduced atmospheric formation of the latter.

(5) Certain Level 2 potential toxic air contaminants (o-cresol, propylene oxide, nitrobenzene, phenol, and vinylidene chloride) may also be precursors for other Level 2 compounds.

1.3.2 Atmospheric Removal

1.3.2.1 Estimation of Reaction Rates

The Level 2 potential toxic air contaminants under study include a wide variety of compounds whose persistence in the atmosphere may be controlled by a number of different reaction pathways. Many of these compounds had not been studied before, and there was little or no information concerning their rates of reaction in the atmosphere and the corresponding reaction products. For these compounds, estimates were made upon the basis of available data for their structural homologues, using structure-reactivity relationships (SRRs) for the relevant atmospheric reactions. Our findings were as follows.

(1) The most important reactions in the atmosphere include photolysis (dissociation of a molecule upon exposure to sunlight), reaction with ozone (O_3), reaction with the hydroxyl radical (OH), and reaction with the nitrate radical (NO_3). The role of each reaction in the removal of each pollutant was investigated.

(2) Measured rate constants were available for only 11 organic-OH reactions, 10 organic-O_3 reactions (of which 9 are negligible for atmospheric removal), and 8 organic-NO_3 reactions (of which 3 are negligible), for a total of 29 reactions.

(3) Using measured ionization potentials and SRRs, rate constants could be estimated for another 63 reactions.

(4) Using estimated ionization potentials and SRRs, rate constants were estimated for all of the remaining reactions of interest, except for those undergone by the dialkyl nitrosamines; however, since nitrosamines photolyze rapidly in sunlight, the lack of OH, O_3 and NO_3 reaction data was not critical.

1.3.2.2 Removal Mechanisms and Products

Table 1.3-2 shows, for each Level 2 compound and compound class, the relative importance of the four main removal mechanisms, along with the observed or predicted reaction products. Note that many of the reaction products are the result of secondary reactions occurring after initial removal of the Level 2 compound of interest; since many of these secondary products are of environmental importance, they have been included in the discussion. The results of our evaluation of atmospheric removal mechanisms are as follows.

(1) For 15 of the Level 2 compounds and compound classes, reaction with OH is clearly the predominant removal mechanism; OH is also important in the removal of another 5 compounds.

(2) Photolysis is the most significant removal mechanism for the dialkyl nitrosamines and nitrosomorpholine, and is important in removing acetaldehyde and acrolein. Its role in removing hexachlorocyclopentadiene is expected, but unconfirmed.

(3) There appear to be no significant chemical removal mechanisms for manganese, mercury, methyl bromide, or phosgene; they leave the troposphere chiefly through diffusion to the stratosphere, washout, and dry deposition.

(4) Ozone reactions do not predominate for any of the Level 2 compounds, although they are important for acrolein, allyl chloride, chloroprene, hexachlorocyclopentadiene, and maleic anhydride.

(5) Reaction with NO_3, which is expected to be important for acrolein, allyl chloride, chloroprene, cresols, hexachlorocyclopentadiene, and phenols, predominates only at night, in the absence of competition from photolysis, OH and O_3.

(6) Formaldehyde, which is a Level 1 toxic air contaminant, is an expected reaction product for 10 of the Level 2 compounds.

(7) Several Level 2 potential toxic air contaminants, including acetaldehyde, nitro- and dinitro-cresols, maleic anhydride,

Table 1.3-2

ATMOSPHERIC REMOVAL OF LEVEL 2 POTENTIAL TOXIC AIR CONTAMINANTS

	Removal Mechanisms[a]				Atmospheric Reaction Products
	$h\nu$	OH	O_3	NO_3	
Acetaldehyde	*	*	-	-	Formaldehyde, peroxyacetyl nitrate (PAN)
Acrolein	+	*	+	+	Formaldehyde, glyoxal, formic acid, glyoxylic acid
Acrylonitrile	-	*	-	-	Formaldehyde, formyl cyanide, HCN
Allyl Chloride	-	*	+	+	Formaldehyde, chloroacetaldehyde, chloro-PAN, formic acid, chloroacetic acid
Benzyl Chloride	-	*	-	-	Peroxybenzoyl nitrate (PBzN), nitrobenzyl chloride, chlorocresols, chlorinated dicarbonyls
Monochlorobenzene	-	*	-	-	Chlorophenol, nitrochlorobenzene, chlorinated dicarbonyls
Chloroprene	-	+	+	+	Acyl chlorides (ClCOCHO, ClCOCOOH), formaldehyde
Cresols	-	*	-	+	OH: nitrocresols, pyruvic acid, PAN; NO_3: nitric acid formed at night
Chlorobenzenes	?	+	-	-	Chlorophenol, nitrochlorobenzene, chlorinated dicarbonyls
Dialkyl Nitrosamines	*	-	-	-	Nitramines, aldehydes, amides
1,4-Dioxane	-	*	-	-	Formaldehyde, CO, CO_2
Epichlorohydrin	-	*	-	-	Formaldehyde, chloroacetaldehyde, chloro-PAN
Glycol Ethers	-	*	-	-	Large number of hydroxy and alkoxy acids, aldehydes, and acetates
Hexachlorocyclopentadiene	?	+	+	+	Oxalyl chloride and other chlorinated products

Table 1.3-2 (Continued)

ATMOSPHERIC REMOVAL OF LEVEL 2 POTENTIAL TOXIC AIR CONTAMINANTS

	Removal Mechanisms[a]				Atmospheric Reaction Products
	$h\nu$	OH	O_3	NO_3	
Maleic Anhydride	-	+	+	?	Dicarbonyls, CO, CO_2, HO_2
Manganese	-	-	-	-	Washout is main removal mechanism
Methyl Bromide	-	*	-	-	Very slow; deposition and upward diffusion are main removal mechanisms
Mercury	-	-	-	-	Washout is main removal mechanism
Nitrobenzenes	-	*	-	-	3-nitrophenol, dinitrobenzene, aliphatic dicarbonyls, phenol
Nitrosomorpholine	*	-	-	-	Nitramines, aldehydes, amides
Phenols	-	+	-	+	Nitrophenols, glyoxal, glyoxylic acid, nitrocresols
Phosgene	-	-	-	-	Very slow; deposition and upward diffusion are main removal mechanisms
Propylene Oxide	-	*	-	-	Formaldehyde, acetaldehyde, CO, PAN
Vinylidene Chloride	-	*	-	-	Formaldehyde, phosgene, formyl chloride (minor), chloroacetyl chloride (?)
Xylenes	-	*	-	-	CO, formaldehyde, glyoxal, methylglyoxal, biacetyl, PAN, methylbenzyl nitrate, tolu-aldehyde, nitro-xylene isomers, dimethyl phenol isomers, others

[a]Symbols denote importance of photolysis ($h\nu$) reaction, with the hydroxyl radical (OH), reaction with ozone (O_3), and nighttime reaction with NO_3:

- * = predominant mechanism
- + = mechanism plays some role in removal
- - = mechanism unimportant in ambient atmosphere
- ? = possible mechanism

nitrophenols, and phosgene, are predicted to form from the chemical removal of other Level 2 compounds.

(8) Other compounds, which are not presently designated as potential toxic air contaminants, but which are nevertheless of health concern, result from the reaction of Level 2 compounds; these include chloroacetaldehyde, formyl cyanide, hydrogen cyanide, nitramines, oxalyl chloride, peroxyacyl nitrates (PAN) and chloro-PAN, and peroxybenzoyl nitrate (PBzN).

1.3.3 Atmospheric Residence Time

Figure 1.3-1 shows the atmospheric half life, in days, of each of the Level 2 compounds and compound classes, assuming the presence of 10^6 molecules-cm^{-3} of OH. From this figure, and other information obtained as part of this study, we may conclude the following:

(1) The most reactive compounds are the dialkyl nitrosamines and nitrosomorpholine, which are removed by photolysis within one or two hours.

(2) The remaining Level 2 compounds may be divided into four groups, on the basis of their reactivity with OH. The shortest-lived group, with half-lives of about 2 to 20 hours, includes acetaldehyde, acrolein, allyl chloride, chloroprene, cresols, 1,4-dioxane, glycol ethers, hexachlorocyclopentadiene, maleic anhydride, phenols, vinylidene chloride, and xylenes.

(3) The second most-reactive group with respect to OH includes acrylonitrile, benzyl chloride, chlorobenzenes, epichlorohydrin, and propylene oxide; their half-lives are several days.

(4) The third group, with half-lives of several weeks, includes the nitrophenols and nitrocresols.

(5) Phosgene, dinitrocresol, methyl bromide, and nitrobenzene are the least chemically reactive in the atmosphere. In the absence of diffusion to the stratosphere, washout by rain, and dry deposition, the half lives of these compounds would be about 8 to 20 months.

(6) Although the atmospheric persistence of most of the Level 2 potential toxic air contaminants is controlled by their reaction with OH, nighttime reaction with NO_3 can dominate in some instances; for example, the half-lives of cresols, hexachlorocyclopentadiene, and phenol, in the presence of 50 ppt of NO_3, would be about 10 minutes.

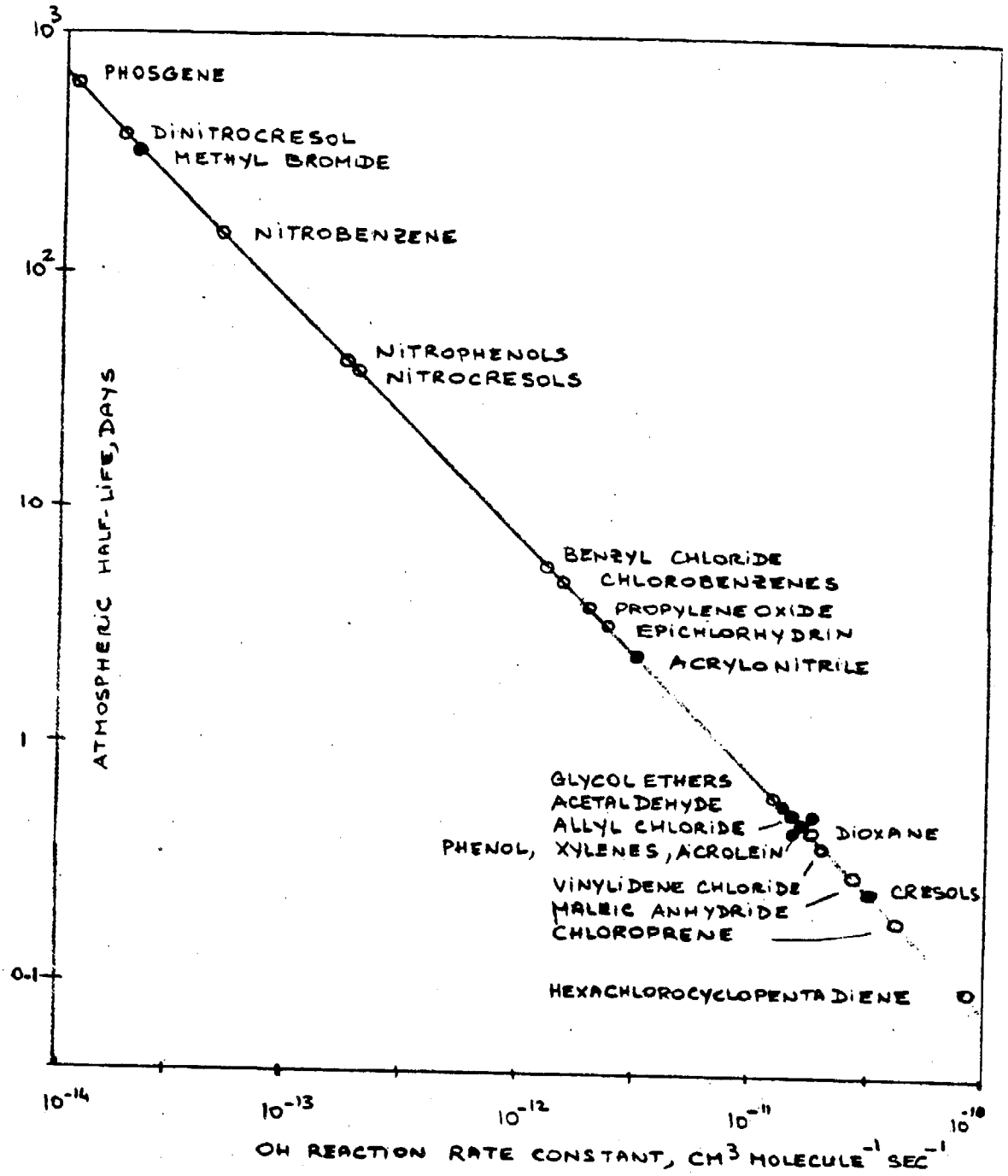

Figure 1.3-1. Atmospheric Removal of Level 2 Compounds by Reaction with OH for OH = 10^6 molecules cm^{-3}. Dark Circles are Measured OH Reaction Rate Constants. Open Circles are Rate Constants Estimated from SRR.

1.4 SELECTION OF COMPOUNDS FOR PHASE II

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.

1.4.1 Ranking Approach

(1) Compounds were first ranked according to amount of emissions, uncertainty in emissions, and uncertainty in ambient concentration data.

(2) Seven compounds rated significantly higher than the others, and were tentatively designated as the "highest priority" group; others were placed into "secondary priority," "lower priority," and "elimination" groups.

(3) All compounds were then rated as to their atmospheric persistence, existence of measurement data for California, and toxicity of degradation products.

(4) Compounds for which at least some California ambient concentration data are available, which form in the atmosphere, and which have high atmospheric persistence or toxic degradation products, were "promoted" from the secondary and lower priority groups resulting from the first ranking step.

1.4.2 Ranking Results

(1) On the basis of California use and emissions, uncertainty in emissions, and uncertainty in ambient concentration data, the following compounds were assigned highest priority: acetaldehyde, acrolein, chlorobenzenes, glycol ethers, monochlorobenzene, methyl bromide, and xylenes. Secondary priority was given to cresols, 1,4-dioxane, phenols, and propylene oxide.

(2) On the basis of their high atmospheric persistence or toxic degradation products, we "promoted" cresols, dialkyl

nitrosamines, phenols and phosgene from lower groups to the highest priority group. Vinylidene chloride, which has been documented in California ambient air, was not promoted, since it has low persistence in the atmosphere and is not a major precursor for ambient phosgene.

(3) The final list of compounds highly recommended for Phase II investigation includes acetaldehyde, acrolein, monochlorobenzene, cresols, chlorobenzenes, dialkyl nitrosamines, glycol ethers, methyl bromide, phenols, phosgene, and xylenes.

2.0
RECOMMENDATIONS

2.1 COMPOUNDS RECOMMENDED FOR PHASE II

We recommend that the following 11 Level 2 compounds 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 are not recommended for further investigation:

- Chloroprene
- Hexachlorocyclopentadiene

2.2 EMISSIONS CHARACTERIZATION

(1) Acetaldehyde, phenols, and xylenes should be added to the set of compounds to be investigated in the upcoming ARB program, "Measurement of Selected Toxic Substances from Gasoline-Powered Light-Duty Vehicles."

(2) Source tests of stationary fossil fuel combustion sources, including industrial and domestic boilers and heaters, should be conducted to develop improved emission factors for acetaldehyde and acrolein.

(3) Source tests should also be conducted at the following facilities:

- PPG Industries, Inc., Irwindale (to determine o,p-dichlorobenzene emissions from production);
- PMC Specialties Group, Inc., Santa Fe Springs (to determine cresol emissions from production);
- Sandia National Laboratory and one or two other cresol users (to develop improved emission factors);
- Feedlots and leather tanneries (to develop emission factors for amine precursors of dialkyl nitrosamines);
- Niklor Chemical Company, Long Beach (to develop emission factors for methyl bromide packaging);

- Stapleton Spence Packing, San Jose (to develop emission factors for use of methyl bromide in food processing); and

- Marine waters off central and southern coasts (to determine the potential for emissions of methyl bromide from biogenic sources)

(4) Industrial surveys should be conducted to obtain information on purchase, incorporation into products, use of formulations, recycling, disposal, and existence and effectiveness of emission control for the following compounds and industries:

- Monochlorobenzene and other chlorinated benzenes (manufacturers of adhesives, paints, polishes, waxes, pharmaceuticals and perfumes, dyes, insecticides, and herbicides);

- Cresols (manufacturers of coated fabrics, metal household furniture, plastics materials and resins, polishes, paints, agricultural chemicals, and industrial machinery; and wood preservers);

- Amine precursors to dialkyl nitrosamines (leather tanneries, users of synthetic cutting fluids);

- Glycol ethers (a wide variety of industries);

- Phenols (electronics, computer manufacturing, and several other industries in the Bay Area and South Coast air basins); and

- Xylenes (a wide variety of industries)

(5) The extent of use of consumer products which contain recommended Level 2 potential toxic air contaminants, including chlorinated benzenes in pesticides, cresols in disinfectants and cleaning products, and glycol ethers and xylenes in a variety of products, needs to be determined.

2.3 AMBIENT SAMPLING

(1) An areawide sampling program should 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, and phosgene.

(2) Recommended methods for collecting and analyzing ambient samples of these compounds are shown in Table 2.3-1.

(3) 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.

(4) 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, should be conducted 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.

(5) Phase II should also include sampling around known point sources of chlorobenzenes, cresols, methyl bromide, and phenols, to ascertain whether population exposure in the neighborhood of the source was significantly higher than elsewhere in the general area; this type of sampling could also be used in conjunction with modeling to "back-calculate" emission rates and therefore confirm emission estimates obtained through source testing or mass balance calculations.

2.4 MODELING

(1) Short-term (i.e. 1-hour, 8-hour or 24-hour) and long-term (annual average) concentrations around selected point sources, should be determined by atmospheric dispersion modeling under

Table 2.3-1

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	<2 - <5	30 - 60
	DNPH-SepPak C18 collection/HPLC	<2	100
Acrolein	DNPH-impinger collection/HPLC	NA[a]	NA[a]
	DNPH-SepPak C18 collection/HPLC	<0.7[b]	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.

worst-case meteorological scenarios in order to assess the potential for significant population exposure.

(2) Basin-wide modeling, using generic point and area emission sources, should be used to identify areas of high potential ambient concentrations.

(3) We recommend the Industrial Source Complex Short-Term model for the short-term modeling and the Climatological Dispersion Model for the annual average modeling.

2.5 LABORATORY STUDIES OF ATMOSPHERIC REACTIVITY

(1) Atmospheric formation and removal processes should be evaluated using small Teflon outdoor chambers and experimental protocols recommended by the U.S. Environmental Protection Agency.

(2) Experiments should include the following (although all may not apply to some compounds):

- A control run, with only the Level 2 compound in pure air in the dark;
- 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 hydroxyl 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.

(3) Table 2.5-1 lists the recommended subjects for laboratory studies for each of the Level 2 potential toxic air contaminants to be investigated in Phase II.

Table 2.5-1

RECOMMENDED LABORATORY STUDIES OF LEVEL 2 COMPOUNDS

Level 2 Compound	Processes to be Studied	
	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.

3.0
INTRODUCTION AND BACKGROUND

3.1 INTRODUCTION

3.1.1 Scope and Objectives

Regulatory agencies at all levels have in recent years been exploring means to reduce public exposure to "toxic" or "hazardous" air pollutants. Although there is no standard definition of a "toxic air pollutant" (Goldstein, 1983), such subtances are regarded by the Clean Air Act as those which may have adverse human health effects and which are not among those for which the U.S. Environmental Protection Agency (EPA) has established a National Ambient Air Quality Standard (Cannon, 1986). Section 39655 of California Assembly Bill 1807, known as "the Tanner Bill," defines a "toxic air contaminant" as:

> "an air pollutant which may cause or contribute to an increase in mortality or an increase in serious illness, or which may pose a present or potential hazard to human health."

Until the early 1980s, regulation of toxic air contaminants was primarily the responsibility of the EPA, which, under Section 112 of the Clean Air Act, was to list and set national emission standards for pollutants which pose a localized risk of adverse human health impacts (Cannon, 1986). It is generally agreed that EPA's programs under Section 112 have not been successful to date in addressing air toxics problems (Hunt and Egan, 1985; Haemisegger et al., 1985; Cannon, 1986). As a result, state and local agencies are playing an increasing role in conducting research and establishing regulatory programs.

The Tanner Bill requires the ARB and the California Department of Health Services to give priority to the evaluation and regulation of substances "based on 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." The ARB staff has to date divided candidate toxic air contaminants into two major classes (CARB, 1985). "Level 1" compounds are those for which sufficient information exists to initiate a full health effects evaluation. Level 2 compounds are those which the ARB considers to be of "potential concern in California." They require additional documentation to determine whether further health effects assessment is needed. In keeping with the ARB's responsibilities under A.B. 1807, the emphasis of the Board's research is to be upon emissions and atmospheric concentrations, rather than upon health effects per se.

In order to determine which, if any, of the Level 2 potential toxic air contaminants merit further consideration under the Tanner Bill process, the ARB is conducting a two-phased research program, of which the present study comprises Phase I. The overall goals of Phase I were to obtain as much information as possible from available sources, to identify data gaps, and to plan more detailed activities, such as source testing, for Phase II. The specific objectives of the present study were:

- To evaluate the potential of listing Level 2 compounds as toxic air contaminants in accordance with the criteria listed in Section 39605 et seq. of the California Health and Safety Code; and
- To identify data deficiencies, provide missing data, and report where such data are not available.

Of the seven issues which the ARB must address in preparing a regulatory report under Section 38665 of the Health and Safety Code, the following three were of concern in this study:

- The rate and extent of present and anticipated future emissions and estimated levels of human exposure;
- The stability, persistence, transformation products, dispersion potential, and other physical and chemical characteristics of the substance when present in the ambient air; and
- The categories, numbers, and relative contribution of present or anticipated sources of the substance, including mobile, industrial, agricultural and natural sources.

Table 3.1-1 lists the Level 2 potential toxic air contaminants as originally defined by the ARB. Several of the entries, such as dialkyl nitrosamines, comprise a large number of individual species. In order to keep the scope of the study manageable, specific compounds were chosen for each of the chemical classes on the basis of preliminary knowledge about their presence in ambient air in California. Table 3.1-2 shows the 45 species decided upon by SAIC and the ARB. The categories "chlorobenzene(s)" and "p-dichlorobenzene" were changed to "monochlorobenzene" and "chlorobenzenes," the latter consisting of those di- and tri-substituted chlorobenzenes which were most volatile and likely to be present in California. The three dialkyl nitrosamines chosen were the most volatile. Although at least six glycol ethers are used commercially in California, previous research (Rogozen et al., 1985) showed only three to be in common use. Inorganic manganese compounds chosen were those which are the most environmentally and/or commercially important. The organic compound methylcyclopentadienyl manganese tricarbonyl (MMT) was selected because of its use as a fuel additive. The only mercury compound studied was elemental mercury (Hg^0), and mononitrobenzene was the only nitrobenzene compound included. Four nitrophenols were included in the phenols group, mainly because of their presence in ambient air; however, use and emissions data were generally available only for phenol.

3.1.2 Outline of the Report

The remainder of this chapter describes the methods used by SAIC and its subcontractor, Daniel Grosjean and Associates, to identify emission sources, estimate emissions, and analyze the atmospheric chemistry of the Level 2 potential toxic air contaminants. Chapters 4 through 28 are dossiers on the 25 compounds and compound classes. Each dossier summarizes information on physical and chemical properties, emission sources, ambient concentrations, and atmospheric formation and removal processes. In Chapter 29, the rationale for recommending further study in Phase II is presented, and the Level 2 compounds are ranked. Sampling and analytical techniques appropriate for the selected compounds are briefly reviewed in Chapter 30. Finally, Chapter 31 outlines a plan to reduce the data gaps identified in Phase I.

Table 3.1-1

ORIGINAL LIST OF LEVEL 2 POTENTIAL TOXIC AIR CONTAMINANTS

Acetaldehyde
Acrolein
Acrylonitrile
Allyl Chloride
Benzyl Chloride
Chlorobenzene(s)
Chloroprene
Cresols
p-Dichlorobenzene
Dialkyl Nitrosamines
1,4-Dioxane
Epichlorohydrin
Glycol Ethers
Hexachlorocyclopentadiene
Maleic Anhydride
Manganese
Methyl Bromide
Mercury
Nitrobenzene(s)
Nitrosomorpholine
Phenol(s)
Phosgene
Propylene Oxide
Vinylidene Chloride
Xylenes

Table 3.1-2

FINAL LIST OF LEVEL 2 POTENTIAL TOXIC AIR CONTAMINANTS

Acetaldehyde
Acrolein
Acrylonitrile
Allyl Chloride
Benzyl Chloride
Monochlorobenzene
Chloroprene
Cresols

- ortho-cresol
- meta-cresol
- para-cresol

Chlorobenzenes

- o-dichlorobenzene
- p-dichlorobenzene
- 1,2,4-trichlorobenzene
- 1,3,5-trichlorobenzene

Dialkyl Nitrosamines

- N-dimethylnitrosamine
- N-diethylnitrosamine
- N-methylethylnitrosamine

1,4-Dioxane
Epichlorohydrin
Glycol Ethers

- Ethylene glycol monomethyl ether
- Ethylene glycol monoethyl ether
- Ethylene glycol monobutyl ether

Hexachlorocyclopentadiene
Maleic Anhydride
Manganese

- Elemental manganese
- Manganese oxide (MnO)
- Manganese dioxide (MnO_2)
- Manganese sulfate ($MnSO_4$)
- Manganese (II, III) oxide (Mn_3O_4)
- Methylcyclopentadienyl manganese tricarbonyl (MMT)

Methyl Bromide
Mercury (elemental)
Nitrobenzene
Nitrosomorpholine
Phenols

- Phenol
- 2-nitrophenol
- 4-nitrophenol
- 3-nitro-2-hydroxytoluene
- 5-nitro-2-hydroxytoluene

Phosgene
Propylene Oxide
Vinylidene Chloride
Xylenes

- ortho-xylene
- meta-xylene
- para-xylene

3.2 METHODS FOR ESTIMATING CALIFORNIA USE AND EMISSIONS

The purpose of this section is to describe the methods used by SAIC to identify facilities and activities in which Level 2 potential toxic air contaminants are used in California, and to estimate point and area source emissions therefrom. In order to assist the ARB in planning further research on the Level 2 compounds, our discussion will include comments on the usefulness of the several approaches taken, as well as judgments as to the quality of the data sources.

3.2.1 Information-Gathering Strategy

The first step in investigating sources of emissions of the 25 Level 2 compounds and compound classes was to divide potential use and emissions into four categories. Direct production was defined as deliberate manufacture or refining, such as synthesis of phenol by peroxidation of cumene. Indirect or incidental production includes the unintentional synthesis or release of a compound during production or processing of something else, such as byproduct formation of maleic anhydride during manufacture of phthalic anhydride. Indirect production also includes formation or release of potential toxic air contaminants such as acrolein or mercury during combustion. (A third form of indirect production, atmospheric synthesis, is discussed in Section 3.3.) Emissions can also occur during industrial use, which includes use of a compound as a feedstock for other products (e.g. use of phenol to make cresylic acid), incorporation of a compound into a product without altering it chemically (e.g. addition of xylenes to paints), or direct use as a solvent. Finally, several of the Level 2 compounds, such as glycol ethers, are found in consumer products, and may be emitted during use thereof.

It was suspected early in the project that only a few of the Level 2 compounds were likely to be produced in California. Nevertheless, considerable effort was devoted to identifying manufacturers and confirming that none had facilities in the state. "Known" California producers were also contacted to verify that they continued to manufacture Level 2 compounds. When we were satisfied that we had confirmed the presence or

absence of California producers, we turned our attention to the potential industrial uses of the compounds. An online data base search, as well as review of several chemical compound compendia (Hawley, 1981; Mackison et al., 1981; Proctor and Hughes, 1978; Sax, 1984; Sittig, 1981), identified major uses of the Level 2 toxic air contaminants. Since many of the compounds have a dozen or more uses, identifying and contacting industrial users was much more difficult and time consuming than identifying producers.

As will be discussed below, emission inventories for most of the Level 2 potential toxic air contaminants had been prepared by the South Coast and Bay Area air quality management districts, and by the U.S. Environmental Protection Agency (EPA). Staff of the EPA's Pollutant Assessment Branch in Research Triangle Park, NC provided us with additional information on several of the compounds. These previously compiled inventories were reviewed critically and major sources listed were contacted to verify use of Level 2 compounds.

Finally, where no inventory data were available, we attempted to estimate emissions of several of the Level 2 compounds. Except for certain types of combustion sources, emission factors were not readily available. In some cases, such as emissions of manganese from sewage sludge combustion, we developed rough emission factors from reported source test data.

Given the large number and variety of the Level 2 potential toxic air contaminants, it was necessary to explore several avenues of research simultaneously. In general, relevant information on a given compound was obtained from more than one source. In keeping with the limited scope of Phase I of this program, we relied heavily on existing information. Wherever possible, however, we independently verified data through direct contacts with chemical producers and users. In addition, some heretofore unavailable information was obtained by SAIC.

3.2.2 Identification of Producers and Users of Level 2 Compounds

3.2.2.1 Online Data Base Searches

Early in the project, SAIC conducted a search of four online data bases:

- Toxicology Data Bank (TDB)
- Chemical Industry Notes (CIN)
- Thomas Register Online
- PTS U.S. Time Series

The Toxicology Data Bank, which is maintained by the National Library of Medicine (NLM, 1981), summarizes information in references such as the Merck Index, Patty's Industrial Hygiene and Toxicology, and the Stanford Research Institute's Chemical Economics Handbook. Included are U.S. production, imports and exports for various years; types of use; percentages of consumption in major end uses; methods of manufacturing, and the names and addresses of principal U.S. manufacturers. The consumption pattern data were quite useful, although in most cases they were from no later than 1981. The data base does not identify users of the compounds.

Chemical Industry Notes, which is provided by Chemical Abstracts Service and the American Chemical Society (Columbus, OH), indexes over 80 journals, newspapers and other periodicals which focus on current events in the chemical industry. Entries begin in 1974 and are updated every two weeks. Its information on trends in chemical production and use was especially useful. CIN also summarizes changes in federal regulations and occasionally refers to environmental issues.

The Thomas Register Online, which is produced by Thomas Publishing Company, Inc. (New York, NY), contains information on about 123,000 U.S. manufacturers of about 50,000 products, and is equivalent to the printed Thomas Register of American Manufacturers. One advantage of this database is that it can be searched by very specific product names, such as epoxy resin,

rather than by more general standard industrial classification (SIC) codes. A disadvantage is that it generally contains data on larger companies, omitting many which were important in this study.

PTS U.S. Time Series contains historical data and forecasts for production and consumption of many compounds. It is provided by Predicasts (Cleveland, OH). Relatively few of the compounds of interest in this study were found in this data base, and most of the information obtained was duplicated in CIN.

3.2.2.2 Directory of Chemical Producers

Producers and users of Level 2 potential toxic air contaminants were also identified through a manual search of the 1983 Directory of Chemical Producers, United States of America (SRI, 1983). The "Products" section of this publication lists, for each chemical or chemical product, the names and locations of each relevant manufacturer. The "companies" section of the directory lists the address and the products manufactured at each facility. This reference proved quite valuable, and provided leads for the telephone and written inquiries described in Section 3.2.3.6 of this report.

3.2.3 Direct Production and Industrial Use and Emissions

Most of the data on industrial production and use of the compounds of interest in California were obtained from the following:

- An industrial survey conducted by the South Coast Air Quality Management District;
- A point-source emission compilation prepared by Radian Corporation for the U.S. Environmental Protection Agency, Region IX;
- A special study conducted by the Bay Area Air Quality Management District;
- A search of the ARB's Emission Data System;
- Computer searches performed by the U.S. Department of the Interior, Bureau of Mines; and

- Letters and telephone calls to known and potential producers and users identified in the Organic Chemical Producers Data Base and the SRI Chemical Economics Handbook

Table 3.2-1 shows which data sources contained or led to information on which of the Level 2 potential toxic air contaminants. It is clear that no single data base was sufficient for the entire evaluation.

3.2.3.1 South Coast Air Quality Management District Inventory

In 1983, the Engineering and Planning divisions of the South Coast Air Quality Management District (SCAQMD) prepared an inventory of 1982 emissions of 30 toxic and/or hazardous compounds in the South Coast Air Basin (Zwiacher et al., 1983). For 20 of the substances, among which were 8 Level 2 compounds, the SCAQMD sent a written questionnaire to 1,606 companies. Facilities were selected by searching the District's Automated Equipment Information System (AEIS) for equipment categories in which the 20 target compounds were believed likely to be used. Respondents were asked to estimate their emissions of the compounds in 1982; when this was not possible, the District used "engineering calculations" to estimate emissions from the data provided. Unfortunately, the basis for these calculations is not reported, and the District's files were generally unavailable for review. (Whatever information on methods which appears in the compound dossiers in Chapters 4 through 28 of this report was obtained from copies of SCAQMD questionnaire forms received by the ARB.) For each compound, results are reported as emissions in lb/year for each facility. A supplemental document (SCAQMD, 1984) shows emissions by standard industrial classification (SIC) code for each pollutant and displays point sources on a gridded map of the SCAB.

3.2.3.2 EPA Region IX Compilation

In 1985 Radian Corporation compiled source-specific data on 51 chemicals, compounds, and compound groups for Region IX of the U.S. Environmental Protection Agency (Bloomhardt and Pelland, 1985). Included were 14 Level 2 compounds. Most of the information was obtained by contacting project officers in EPA's Pollutant Assessment Branch (PAB) in

Table 3.2-1

DATA SOURCES APPLICABLE TO LEVEL 2 TOXIC AIR CONTAMINANTS

Compound Group	SCAQMD	EPA Region IX	BAAQMD	ARB	Bureau of Mines	OCPDB
Acetaldehyde		X	X	X		
Acrolein		X	X	X		X
Acrylonitrile	X	X	X			X
Allyl Chloride			X			
Benzyl Chloride			X			
Monochlorobenzene		X	X	X		X
Chloroprene		X	X			
Cresols			X			X
Chlorobenzenes			X			
Dialkyl Nitrosamines			X			
1,4-Dioxane	X		X			
Epichlorohydrin	X	X	X			X
Glycol Ethers						
Hexachlorocyclopentadiene		X	X			
Maleic Anhydride	X		X	X		X
Manganese		X	X	X	X	
Methyl Bromide	X		X			
Mercury	X	X	X	X	X	
Nitrobenzenes			X			
Nitrosomorpholine			X			
Phenol		X	X	X		X
Phosgene		X	X			
Propylene Oxide	X	X	X			
Vinylidene Chloride		X	X			X
Xylenes	X		X			X

Source: SCAQMD = Zwiacher et al. (1983); EPA Region IX = Bloomhardt and Pelland (1985); BAAQMD = Hill (1985); ARB = Newby (1986); Bureau of Mines = Carrico (1986); OCPDB = Waterman (1985).

Research Triangle Park, NC and then reviewing unpublished data and recently published reports. For each toxic substance, Radian reports the relevant source categories; specific sources and/or plant names and locations; relevant air pollution control district; emissions from processing, storage and fugitive sources; origin of emission estimates; modeled ambient concentrations, and health risks. One important limitation of this study was that it examined only materials on hand at the PAB (Pelland, 1986). In attempting to verify the inventory, we found that much of the California-specific information was obsolete or incorrect. Subsequent discussions with EPA staff confirmed that some of the data had been obtained in the 1960s and 1970s and had not been recently verified (Lahre, 1986; Pate, 1986).

3.2.3.3 Bay Area Air Quality Management District Study

In 1984 and 1985, the Bay Area Air Quality Management District (BAAQMD) conducted a two-part survey of all facilities having District permits, except for gasoline dispensing facilities and dry cleaners (Hill, 1985). In the first part, a "screening survey," the District sent each facility a list of 50 organic compounds and isomers, including all of the Level 2 compounds except glycol ethers. Respondents were asked to indicate whether any of the compounds were purchased, packaged, manufactured, used as intermediates, or present in incinerators. Of the 874 companies contacted, 389 indicated that no toxic air contaminants were present, 438 responded that toxics were present, and 47 did not reply. The BAAQMD found that facilities failed in many cases to indicate use of a compound when it was present as an ingredient of a formulation, such as xylene in paint. Also, many respondents apparently did not understand the meaning of the term "intermediate."

The District then used the results of the screening survey to tailor follow-up usage survey forms for each responding facility. Facilities were asked to report quantities of each substance purchased in 1983 (as pure substance or component of a mixture), incorporated in products, and incinerated. Information on the concentration of the pollutant in incinerator emissions was also requested. Usage values were converted by

BAAQMD staff into emission estimates on the basis of "certain assumptions regarding the processes in use at the sources;" methods for calculating emissions are not reported. The report includes a breakdown of point sources and emissions for each chemical, and a list of sources and toxic substances by three-digit standard industrial classification (SIC) code.

As noted by Hill (1985), substantial follow-up work is required to refine the preliminary estimates and to establish toxic air contaminant control priorities. In particular, information from approximately 1,000 plants which have received permits since 1984 should be incorporated. Also, data from area sources are presently not included in the inventory.

3.2.3.4 Search of the ARB's Statewide Emission Inventory

The ARB's statewide emission inventory does not generally contain information on specific toxic air contaminants. However, we believed that some of the facility, throughput, and emission data could be used, in conjunction with data from other sources, to estimate point-source emissions of certain Level 2 compounds. In December 1985, SAIC requested the Emission Inventory Branch to search the emission inventory for the combinations of SIC code and source classification code (SCC) shown in Table 3.2-2 and to report, for each facility,

- Facility name, address, telephone number and contact;
- Process rate upon which the emissions are based;
- Uncontrolled and controlled emission factors for total organic gases (TOG); and
- Emissions of TOG by the most disaggregated level of speciation available in the inventory.

The SCC numbers, which were chosen from a list published by the U.S. Environmental Protection Agency in Volume V of the AEROS Manual of Codes (USEPA, 1981), were believed *a priori* to correspond to processes in which Level 2 compounds were produced or used as feedstock. The combinations of SCC and SIC code all appeared in the March 1982 revision of the ARB's Emission Data System Review and Update Report Manual (CARB, 1982), and were

Table 3.2-2

CRITERIA FOR SEARCH OF STATEWIDE EMISSION INVENTORY

Source Classification Code	SIC Code	Description	Level 2 Compounds
3-01-100-XX[a]	2821	Maleic anhydride in rubber/plastics manufacturing	Maleic anhydride
3-01-019-03	2821	Phthalic anhydride in rubber/plastics formulation	Ortho-xylene
3-01-008-99	2819	Chloro-alkali production	Mercury
3-01-018-01	2821	Polyvinyl chloride manufacturing	Benzyl chloride
	3079	Polyvinyl chloride use in rubber and plastics fabrication	Benzyl chloride
3-01-018-05	2821	Phenolic resin manufacturing	Phenol
3-02-002-XX[a]	2095	Coffee roasting	Acrolein Acetaldehyde
5-01-005-06	4952	Sewage sludge incineration	Chlorobenzene Manganese Mercury

[a]Last two digits may have any value from 01 to 99.

thus believed to apply to at least some facilities in the statewide emission inventory. The ARB search found entries in the statewide emission inventory for 13 coffee roasting facilities, 2 polyvinyl chloride manufacturers, 4 polyvinyl chloride users, 1 maleic anhydride user, 1 phenolic resin manufacturer, and 1 sewage sludge incinerator (Newby, 1986). The only information which proved useful, and was not duplicated by other sources, was the identification of coffee roasters. Even then, process rate data on the larger roasters were coded as "not valid." Furthermore, although the ARB has some speciation data, it does "not consider them reliable for identifying potentially toxic air contaminants or for estimating emissions from these compounds" (Newby, 1986).

3.2.3.5 U.S. Bureau of Mines

At SAIC's request, a mercury specialist at the U.S. Bureau of Mines provided us with a computer listing of the names and addresses of 10 California firms which had reported consumption or processing of mercury in the past few years (Carrico, 1986). The list included a handwritten update detailing the specific uses of the mercury and stating whether any use had been reported for 1984. Attempts were made to contact all of the firms listed by the Bureau of Mines.

3.2.3.6 Additional Research by SAIC

Letters to Producers

Early in the survey, we used the Chemicalweek Buyers' Guide (Chemical Week, 1985) and other industry directories to determine the names of chemical manufacturers and formulators--nationwide--who produce products for which Level 2 compounds are feedstocks and/or ingredients. This review identified 196 firms. Each firm was sent a letter which included the name of the product(s) and the compound(s) of interest, and asked whether it had any manufacturing plants in California and whether the compound(s) of interest were indeed used in the state. Plant capacity data were also requested. A sample letter is shown in Figure 3.2-1. Responses were received from 93 of the firms, none of which reported using Level 2 compounds in manufacturing

SAIC

Science Applications International Corporation

22 September 1985

Perkins Industries, Inc.
6405 Metcalf, Suite 422
Overland Park, KS 66202

Subject: Request for Information on Chemicals for California Air Resources Board Study (Contract No. A4-115-32).

Dear Sir:

Science Applications International Corporation (SAIC) is under contract with the California Air Resources Board (ARB) to investigate the potential for emissons of various chemical compounds to the ambient air of California. One of the objectives of this investigation is to obtain background information on the use of these chemicals in California. This research study does not concern the regulatory aspects of these compounds.

According to the Chemical Week Buyers Guide and/or other industry directories, your company manufactures a product or products which use(s) as an ingredient, intermediate, or feedstock one or more of the chemicals which we are evaluating. We need information on whether you manufacture any of the following products in California and whether any of the chemicals in the second list are used as ingredients or intermediates in the manufacturing process for these products. We would greatly appreciate it if you could take just a moment to answer a few questions about several manufactured products.

Does your firm manufacture any of these products in California?

1. Phenolic resins

If so, are any of the following chemicals used as ingredients, intermediates or feedstocks in the manufacture of one or more of the above products?

1. Phenol

Where are the manufacturing plants located in California and what are their annual production capacities for the above listed products? Finally, whom may we contact for additional technical information about the production of phenolic resins at your plants?

We would appreciate a response even if your firm does not manufacture any of the listed products. Thank you for your assistance in this research. If you have any quesions, please contact me or the principal investigator, Dr. Michael Rogozen, at (213) 318-2611. The ARB research contract monitor is Mr. Joseph Pantalone, who may be reached at (916) 323-1535.

2615 Pacific Coast Highway, #300 Hermosa Beach California 90254 (213) 318-2611

Other SAIC Offices Albuquerque Ann Arbor Arlington Atlanta Boston Chicago [illegible] Los Angeles McLean Palo Alto Santa Barbara Sunnyvale and Tucson

Figure 3.2-1. Example of Letter Sent to U.S. Producers of Level 2 Potential Toxic Air Contaminants.

facilities in California.

OCPDB Survey

The Organic Chemical Producers Data Base (OCPDB) is an automated chemical industry information system developed in 1976 for the U.S. Environmental Protection Agency (Wilkins et al., 1980). It currently contains information on chemical properties, uses, production methods and volumes and toxicity for about 600 chemicals and about 1,300 producing facilities (Lee, 1981). A feature of the OCPDB which is particularly helpful for a study of this type is that the feedstocks for many of the chemicals are listed; thus one can find chemicals for which the Level compounds are feedstocks or intermediates. Figure 3.2-2 shows a typical entry. The system was last updated in September, 1982 (Stutsman, 1985).

A printout of the latest version of the OCPDB was obtained from the EPA's Industrial Environmental Research Laboratory in Cincinnati, OH. We began by searching for all facilities having a California address. (Another helpful feature of this data base is that it lists facilities rather than corporate headquarters or sales offices.) Entries for these facilities were then screened to determine whether Level 2 potential toxic air contaminants were likely to be produced or used. This search identified 54 California facilities in which 10 Level 2 compounds could potentially be produced or used. We attempted to contact these facilities by telephone. Each facility which acknowledged producing or using a Level 2 compound was sent a letter requesting a written confirmation and additional data on production capacity, production, and feedstock use. About one third of the companies responded, and most of them provided useful data.

3.2.4 Indirect Production

The principal sources of indirect production of Level 2 potential toxic air contaminants in California are combustion of fossil fuels and incineration of sewage sludge and other wastes. Information on mobile source emissions of acetaldehyde, acrolein, manganese and dialkyl nitrosamines was obtained primarily through a literature review. In addition, the U.S.

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ORGANIC CHEMICAL PRODUCERS DATA BASE

PRODUCT DATA REPORT

3120 PROPYLENE OXIDE

CAS REGISTRY NUMBER 75569
WISWESSER LINE NOTATION: T3OTJ B
NIOSH NUMBER TZ29750

SYNONYMS

METHYL ETHYLENE OXIDE
NCI-C50099
1,2-EPOXYPROPANE
PROPENE OXIDE
1,2-PROPYLENE OXIDE
EPOXYPROPANE
METHYLOXIRANE
3-METHYL-1,2-EPOXYPROPANE
PROPYLENE EPOXIDE

ECONOMIC DATA

YEAR	VOLUME (MMLBS/YR)	SALES (MM$/YR)	UNIT COST ($/LB)
81			.350
80	1767.170		
71		35.655	
78	2000.000		
79			.240
77	1900.000		

USES (FOR DERIVATION OF CHEMICALS AND ALLIED PRODUCTS)

		AMOUNT (MMLBS/YR)	% DOM.	IPPEU	SIC
			2.000		2869
DIPROPYLENE GLYCOL	INDUSTRIAL ORGANIC CHEMICAL N.E.C.	525.000	25.000	6/287	2869
PROPYLENE GLYCOLS	INDUSTRIAL ORGANIC CHEMICAL N.E.C.			6/149	2869
GLYCOL ETHERS	INDUSTRIAL ORGANIC CHEMICAL N.E.C.				2869
ISOPROPANOLAMINES	INDUSTRIAL ORGANIC CHEMICAL N.E.C.				2865
PROPYLENE CARBONATE	INDUSTRIAL ORGANIC CHEMICAL N.E.C.				2869
HYDROXYPROPYL CELLULOSE	INDUSTRIAL ORGANIC CHEMICAL N.E.C.				2869
HYDROXYPROPYL STARCH	INDUSTRIAL ORGANIC CHEMICAL N.E.C.				2851
NITROCELLULOSE LACQUER	PAINT PRODUCT AS STABILIZER				
GLYCEROL	INDUSTRIAL ORGANIC CHEMICAL N.E.C.			6/252	2869
POLYPROPYLENE GLYCOLS	INDUSTRIAL ORGANIC CHEMICAL N.E.C.			6/288	2869

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ORGANIC CHEMICAL PRODUCERS DATA BASE

PRODUCT DATA REPORT

USES (FOR OTHER COMMERCIAL/INDUSTRIAL APPLICATIONS)

		AMOUNT (MMLBS/YR)	% DOM.	SIC
AGRICULTURAL SERVICE	FUMIGANT			700

PROCESS DESCRIPTION

51 CHLOROHYDRIN PROCESS
IPPEU 6/286

REACTION COMPONENTS	OCPDB #	ICPDB #	INDUSTRIAL ORIGIN	SIC
PROPYLENE CHLOROHYDRIN	3100		INDUSTRIAL ORGANIC CHEMICAL N.E.C.	2869
CALCIUM HYDROXIDE		580	INORGANIC CHEMICAL N.E.C.	2819

A DILUTE PROPYLENE CHLOROHYDRIN SOLUTION IS MIXED WITH A 10% SLURRY OF LIME AND PUMPED TO A STEAM-HEATED FLASH HYDROLYZER FOR CONVERSION TO PROPYLENE OXIDE.

PRODUCING PLANTS

1250	BASF WYANDOTTE CORP.		175.000 MMLBS./YR.
	WYANDOTTE	MI 48192	
	WAYNE	123	
	DETROIT	4090004	
3370	DOW CHEMICAL U.S.A.		340.000 MMLBS./YR.
	PLAQUEMINE	LA 70764	
	IBERVILLE	106	
	LOWER GRAND	0070300	
3400	DOW CHEMICAL U.S.A.		1000.000 MMLBS./YR.
	FREEPORT	TX 77541	
	BRAZORIA	216	
	AUSTIN - OYSTER	12040205	
7870	OLIN CORP.		130.000 MMLBS./YR.
	BRANDENBURG	KY 40108	
	MEADE	104	
	BLUE - SIMKINS	5140104	

Figure 3.2-2. Typical Entry in Organic Chemical Producers Data Base.

Environmental Protection Agency's Office of Mobile Source Air Pollution Control in Cincinnati, OH and its Atmospheric Science Research Laboratory in Research Triangle Park, NC provided us with internal reports and other unpublished data on mobile source emissions tests. Information on stationary combustion sources was obtained through a literature review and from the EPA's Office of Air Quality Planning and Standards, Pollutant Assessment Branch, Research Triangle Park, NC. These data sources are referenced in the compound dossiers, where applicable.

3.2.5 Consumer Use and Emissions

Our original plan in evaluating consumer use of Level 2 potential toxic air contaminants was to:

- Identify classes of consumer product formulations (e.g. household cleaners, personal care products) in which each compound is used as an ingredient;
- Obtain national estimates of the use of each class of formulation;
- Apportion the use of each formulation to California;
- Determine ranges of concentrations of each Level 2 compound in each type of consumer product; and
- Multiply product use rates time the toxic compounds' mass or volumetric concentrations to yield use estimates.

This was essentially the procedure used in a previous SAIC study of organic solvent use and emissions in California (Rogozen et al., 1985) and in a recent consumer product study for the U.S. Environmental Protection Agency (Jones et al., 1986). Early in the present project, SAIC used various compilations of data on chemical compounds (Hawley, 1981; Mackison et al., 1981; Proctor and Hughes, 1978; Sax, 1984; Sittig, 1981), as well as the Toxicology Data Bank search results described in Section 3.2.2, to identify relevant consumer product classes. In addition, we obtained three status reports from the Consumer Product Safety Commission's System for Tracking Inventory of Chemicals (STIC) (CPSC, 1985). Although the main focus of the STIC is upon toxicological data and regulatory status, one of the reports did include limited information on consumer use of some of the Level 2 compounds.

However, most of this information was available from other sources. Several formularies such as Clinical Toxicology of Commercial Products (Gosselin et al., 1984) were then reviewed.

At this point it became apparent that the plan outlined above could not be fully carried out within the resource constraints of Phase I. First, most of the consumer product classes associated with Level 2 toxic air contaminants were rather general, and comprised anywhere from a half dozen to hundreds of specific consumer products. For each product, there may be up to a dozen formulations, many (if not most) of which are proprietary. Not all of the formulations contain the same proportion of the compound(s) of interest. For example, we determined that window and glass cleaners may contain glycol ethers. A search of two formularies (Gosselin et al., 1984; Kline, 1982) identified seven formulations for window and glass cleaners (which are not necessarily all of those presently on the market); four of these contain glycol ethers at from 0.1 to 11 percent by weight, while the other three do not contain any. Information on the market shares of the seven formulations was available only at a prohibitively high cost. Finally, many formulations tend to change over the years. Given the lack of data on the relative importance of each formulation, and the two orders-of-magnitude variation in glycol ether content among formulations, any estimate of use of glycol ethers in this consumer product class would be highly questionable. The same was true for other uses of Level 2 toxic air contaminants in other product classes.

The estimation approach had been fairly successful in the previous ARB organic solvent study because the solvents investigated were in wide use, and their weight percentages did not vary as much from product to product. In the EPA consumer product study, only aggregate levels of photochemically reactive compounds were needed, so the product-to-product variability in individual species composition did not matter. In this study of Level 2 potential toxic air contaminants, we decided that applying the approach would consume time and resources that could better be applied elsewhere.

It was possible, however, to update the ARB organic solvent study's estimates of emissions of glycol ethers and ortho-xylene from applications of

paints and coatings. The previous study had used data on coating solvent composition and use from a data base prepared by SRI International for the National Paint and Coatings Association. For the present investigation, we obtained an updated (1981) version (Connolly et al., 1982) and used more recent data on population, housing units, registered automobiles and other apportionment variables to apportion national use to California.

3.3 METHODS FOR EVALUATION OF ATMOSPHERIC CHEMISTRY

3.3.1 General Considerations

3.3.1.1 Introduction

Chemical reactions play a critical role in the overall persistence of toxic organics in the atmosphere. Ambient concentrations of toxic air contaminants reflect the complex interplay between atmospheric sources and sinks. Sources include direct emissions as well as in-situ production in the atmosphere by gas phase or heterogeneous reactions. Sinks include gas phase reactions, scavenging by hydrometeors, and dry deposition. All these processes take place during dispersion and transport and have strong spatial, seasonal and diurnal variations. In-situ production of toxic air contaminants also varies with spatial and temporal variations in the emissions of the corresponding precursors (e.g. toluene for cresols, butadiene for acrolein).

On first examination, the Level 2 toxic air contaminants under study include a wide variety of compounds whose persistence in the atmosphere may be controlled by a number of different reaction pathways. Many of these compounds have not been studied before, and there is little or no information concerning their rates of reaction in the atmosphere and the corresponding reaction products. Thus, estimates must be made for these compounds on the basis of available data for their structural homologues. Our approach involves the use of structure-reactivity relationships (SRRs) for the relevant atmospheric reactions. In this section, we first define the Level 2 contaminants according to structural classes; we identify reactions and species that are important in the atmospheric removal of each structural

group; and we briefly describe the corresponding reaction mechanisms. Next, we introduce the concept of SRR, and derive SRRs for important atmospheric reactions. We then use these SRRs to verify the consistency of kinetic data for Level 2 contaminants when available, and to estimate reaction rate constants that have not been measured. In turn, this information serves as a basis for a critical evaluation, presented in Chapters 4 to 28, of the ambient concentration and atmospheric persistence of each Level 2 compound.

3.3.1.2 Structural Classification of Level 2 Contaminants

Level 2 contaminants are listed in Table 3.3-1 according to structural similarities. Aromatic compounds contain a benzene ring (C_6H_6) on which one or more hydrogen atoms are replaced by other atoms or functional groups, e.g. chlorobenzene (C_6H_5Cl), nitrobenzene ($C_6H_5NO_2$), 2-nitrophenol ($OH\text{-}C_6H_4\text{-}NO_2$), or hexachlorobenzene (C_6Cl_6). Aliphatic compounds do not contain a benzene ring. The Level 2 aliphatics can be further divided into saturated and unsaturated compounds. The unsaturated compounds include at least one carbon-carbon double bond, $>C{=}C<$, e.g. acrolein ($CH_2{=}CHCHO$), vinylidene chloride ($CH_2{=}CCl_2$), and chloroprene ($CH_2{=}\underset{Cl}{C}\text{-}CH{=}CH_2$). The saturated compounds do not contain $>C{=}C<$ bonds but may include one or more other functional groups including carbonyl (C=O), epoxide ($C\overset{O}{\text{-}}C$), ether (-C-O-C-), and nitroso (-C-N-NO).

3.3.2 Important Atmospheric Reactions

Reactions of importance in the atmosphere include photolysis, reaction with ozone, reaction with the hydroxyl radical, and reaction with the nitrate radical. Photolysis involves dissociation of a molecule upon exposure to sunlight, e.g. $AB + h\nu \rightarrow A + B$, where A and B can be molecules or free radicals. Free radicals contain an odd (unpaired) electron and include atoms (e.g. chlorine atoms, $\dot{Cl}$), groups of atoms (e.g. hydroxyl radical $\dot{HO}$, nitrate radical $\dot{NO_3}$), and molecules. The ubiquitous pollutants nitric oxide (NO) and nitrogen dioxide (NO_2) are free radicals.

Table 3.3-1

STRUCTURAL CLASSIFICATION OF LEVEL 2 CONTAMINANTS

Aromatic Compounds:

- Benzyl chloride
- Chlorobenzenes
  - monochlorobenzene
  - p-dichlorobenzene
  - trichlorobenzene
  - hexachlorobenzene
- Cresol (ortho, meta, para)
- Nitrobenzene
- Phenols
  - phenol
  - 2-nitrophenol
  - 4-nitrophenol
  - 3-nitrocresol
  - 5-nitrocresol
  - 2,4-dinitrocresol
- Xylenes (ortho, meta, para)

Aliphatic Compounds, Unsaturated:

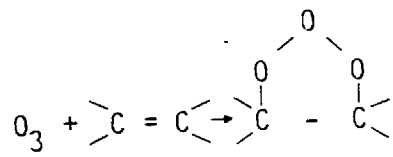
- Acrolein
- Acrylonitrile
- Allyl chloride
- Chloroprene
- Hexachlorocyclopentadiene
- Maleic anhydride
- Vinylidene chloride

Aliphatic Compounds, Saturated:

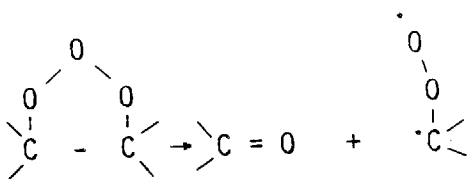
- Acetaldehyde
- Dialkylnitrosamines (dimethyl, diethyl, methyl-ethyl)
- 1,4-dioxane
- Epichlorohydrin
- Glycol ethers
  - ethylene glycol monomethyl ether
  - ethylene glycol monoethyl ether
  - ethylene glycol monobutyl ether
- Methyl bromide
- Nitrosomorpholine
- Phosgene
- Propylene oxide

3.3.2.1 Reaction With Ozone

Reaction with ozone is important for all unsaturated aliphatics, and involves addition of ozone on the carbon-carbon double bond to form a 1,2,3-trioxolane:



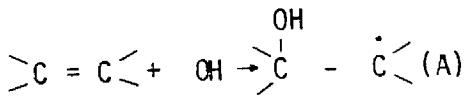
followed by rapid unimolecular decomposition to give a carbonyl compound and a peroxycarbene biradical (the Criegee biradical):



Further reactions of the Criegee biradical include decomposition, rearrangement to a carboxylic acid, or reaction with other pollutants to form a carbonyl (e.g. $H_2\dot{C}\dot{O}O$ from ethylene $\rightarrow H_2 + CO_2$, $H_2O + CO$; $H_2\dot{C}\dot{O}O \rightarrow HCOOH$, formic acid; $H_2\dot{C}\dot{O}O + NO \rightarrow NO_2 + H_2CO$, formaldehyde). These reactions are discussed in further detail in Chapters 4 through 28 for each unsaturated Level 2 compound.

3.3.2.2 Reaction With the Hydroxyl Radical

While reaction with ozone involves only addition, reaction with the hydroxyl radical (OH) may involve both addition and abstraction. The OH-olefin reaction involves OH addition:



followed by reaction of the alkyl radical (A) with O_2 to form an <u>alkylperoxy radical</u> $A\dot{O}_2$. In polluted atmospheres containing NO, peroxy radicals are rapidly converted to <u>alkoxy</u> radicals, i.e. $A\dot{O}_2 + NO \rightarrow A\dot{O} + NO_2$, followed by unimolecular decomposition and other reactions discussed in Chapters 4 through 28. For saturated aliphatics, the OH reaction involves <u>hydrogen atom abstraction</u>:

$$RH + OH \rightarrow H_2O + \dot{R}$$

followed by the alkyl → peroxy → alkoxy sequence discussed above, i.e. $\dot{R} + O_2 \rightarrow R\dot{O}_2$, $R\dot{O}_2 + NO \rightarrow R\dot{O} + NO_2$. For aliphatics containing only one hydrogen atom, only one pathway will be involved, e.g. chloroform, $CHCl_3 + OH \rightarrow H_2O + \dot{C}Cl_3$. For aliphatics containing several hydrogen atoms, the reaction will involve the <u>weakest C-H bond</u>. A list of typical bond strengths is given in Table 3.3-2. Thus, for aldehydes, OH abstraction will involve the weak carbonyl hydrogen, e.g. $CH_3CHO + OH \rightarrow H_2O + CH_3\dot{C}O$. For paraffins, abstraction will involve <u>several pathways</u> reflecting the strength of the C-H bonds, i.e. primary > secondary > tertiary, e.g.:

$$OH + \begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!> CH - CH_2 - CH_3 \rightarrow (CH_3)_2\,\dot{C}\,CH_2\,CH_3 \quad \text{major}$$

$$\rightarrow (CH_3)_2\,CH\,\dot{C}H\,CH_3 \quad \text{some}$$

$$\rightarrow (CH_3)_2\,CH\,CH_2\,\dot{C}H_2 \quad \text{minor}$$

$$\rightarrow \begin{matrix} \dot{C}H_2 \\ CH_3 \end{matrix}\!\!> CH\,CH_2\,CH_3 \quad \text{minor}$$

Table 3.3-2

BOND ENERGIES

Bond	kcal/mole at 25°C
C - H	99 (primary H)
C - H	95 (secondary)
C - H	92 (tertiary)
C - C	80
C = C	150
C - N	62
N = O	145
C ≡ N	213
C - O	81
C = O	175
N - H	84
N - N	35
C - Cl	77
C - Br	64
O - H	110

Reaction with OH may involve <u>both addition and abstraction</u> pathways. This is the case for aromatics, e.g. toluene:

$$C_6H_5 - CH_3 + OH \rightarrow H_2O + C_6H_5\dot{C}H_2 \qquad \text{[abstraction]}$$

$$\rightarrow (CH_3 - C_6H_5OH)^{\cdot} \rightarrow \text{products} \qquad \text{[addition]}$$

3.3.2.3 Reaction With the Nitrate Radical

Reactions involving the nitrate radical are analogous to those involving OH, i.e. addition for unsaturated compounds and hydrogen atom abstraction for saturated compounds, e.g.:

$$RH + NO_3 \rightarrow HNO_3 + \dot{R} \qquad \text{[abstraction]}$$

$$>C = C< + NO_3 \rightarrow >C(NO_3) - \dot{C}< \text{ products} \qquad \text{[addition]}$$

However, little is known regarding the details of the initial NO_3 attack, the subsequent reaction pathways, and the corresponding reaction products.

A few additional definitions not introduced using the above examples need to be mentioned here. Rate constants measured correspond to those of the rate determining step, i.e. the slowest elementary reaction in a given reaction sequence. For addition reactions, the rate determining step is that of initial attack, e.g. $>C = C< + O_3$ trioxolane or $>C = C< + OH \rightarrow >\dot{C} - C(OH)<$ <u>Abstraction reactions, however, often involve a rate-determining addition step</u> followed by rapid decomposition of the adduct, e.g.:

$$RH + OH \rightarrow (RHOH)^{\neq} \rightarrow \dot{R} + H_2O$$

This has implications for the discussion of <u>substituent effects</u> on a given reaction rate. Free radicals, including ozone (a biradical, schematic struc-

ture $^{\cdot}\bar{\underline{O}}-\bar{\underline{O}}-\bar{\underline{O}}^{\cdot}$), the hydroxyl radical ($^{\cdot}\bar{\underline{O}}-H$) and the nitrate radical (NO_3), are all electron-deficient species and will readily react with electron-rich reaction centers. O_3, OH and NO_3 are electrophiles. The reactions of ozone, OH and NO_3 with unsaturated compounds are electrophilic additions, and their reaction rates will closely reflect the electronic density at the reaction center. Thus, reaction rate constants will increase for electron-donating substituents (e.g. methyl, $k\ CH_3CH{=}CH_2 + O_3 = 8 \times k\ CH_2{=}CH_2 + O_3$), and decrease for electron-attracting substituents (e.g. chlorine atoms, $k\ CH_2{=}CHCl + OH = 0.8\ k\ CH_2{=}CH_2 + OH$). Abstraction reactions, if involving a rate determining addition step, will exhibit the same trend as electrophilic addition reactions with respect to substituent effects.

3.3.3 Reaction Rates

The rate of removal of a Level 2 potential toxic organic contaminant from the atmosphere due to chemical reactions can be expressed by:

$$-d(\text{organic})/dt = k_1\ (\text{organic}) + \sum_{i=2,n} k_i\ (\text{organic})(X_i)$$

where k_1 is the photolysis rate constant and k_i are the rate constants for reactions with all pollutants X_i including ozone, hydroxyl radical, etc. With this equation, chemical removal rates can be calculated knowing the ambient levels of the reactive species X_i and the corresponding reaction rate constants. Atmospheric persistence is often defined as the atmospheric half-life, i.e. the time required for the contaminant concentration to reach half of its initial value. Thus, for a single removal process:

$$-d(\text{organic})/dt = k_x\ (\text{organic})(X)$$

Integrating and setting $(\text{organic})_t = 1/2\ (\text{organic})_{t_0}$ yields:

$$\text{half life} = t_{1/2} = \ln 2/k_x(X) = 0.69/k_x(X)$$

As an example, let us calculate the half life of ethylene in a moderately polluted atmosphere:

Reaction	Rate Constant (cm^3 $molecule^{-1}$ sec^{-1})	Average Concentration (molecules cm^{-3})	$t_{1/2}$ (days) day	night
Photolysis	0	-	∞	∞
Ozone	1.6×10^{-18}	2.4×10^{12} (0.1 ppm)	2.0	2.0
OH	0.8×10^{-11}	2.0×10^{6} (0.08 ppt)	0.5	0
NO_3	6.1×10^{-17}	1.2×10^{9} (50 ppt)	0	109

Daytime removal of ethylene will be controlled by its reaction with OH (80 percent) and to a lesser extent with ozone (20 percent), with a composite half-life of 0.4 day. The nitrate radical photolyzes rapidly in sunlight and is not taken into account in the daytime calculations. Removal of ethylene at night will be due to its reaction with ozone (OH radical concentrations are assumed to be negligible at night), along with a very small contribution from reaction with the NO_3 radical.

The above calculations can be extended to all organic contaminants and all species known to react with these organics in the atmosphere. A compilation of literature data has been carried out, and includes several hundred published rate constants for the gas phase reactions of organics with ozone, the hydroxyl radical, the nitrate radical, atomic oxygen (O(3P)), the HO_2 radical, chlorine atoms, and nitrogen dioxide. Reactions with O(3P), HO_2, and NO_2 are of negligible importance in polluted air. The first two species react rapidly with organics including olefins, but their atmospheric concentrations are quite low. The opposite is true of NO_2, i.e. higher ambient concentrations but slower reaction rates. Reactions of organics with chlorine atoms are typically 10 times faster than the corresponding OH reactions. Thus, chlorine atoms would be important if present in urban air at levels of 5×10^4 radicals cm^{-3}, i.e. about one tenth of urban OH levels. No data are available for the levels of chlorine atoms in urban air, and this reaction was not further considered. This leaves us with ozone, OH and NO_3, for which reaction rate constants are summarized in Table 3.3-3 for each

Table 3.3-3

RANGE OF RATE CONSTANTS FOR THE GAS PHASE REACTIONS OF O_3, OH, AND NO_3 WITH ORGANIC COMPOUNDS

(Units: $cm^3 molecule^{-1} sec^{-1}$)

	Ozone	Hydroxyl Radical	Nitrate Radical
Unsaturated Aliphatics:			
Alkenes, cycloalkenes, dienes and cyclodienes	$1.6 \times 10^{-18} - 1.5 \times 10^{-15}$	$8 \times 10^{-12} - 2.1 \times 10^{-10}$	$6.1 \times 10^{-17} - 3.4 \times 10^{-11}$
Haloethenes	$<2 \times 10^{-23} - 2.1 \times 10^{-18}$	$0.17 - 6.8 \times 10^{-12}$	no data
Saturated Aliphatics:			
Alkanes and cycloalkanes	$1\text{-}9 \times 10^{-24}$	$1 \times 10^{-14} - 8.0 \times 10^{-12}$	no data
Ethers, esters, alcohols, epoxides	-	$3.4 \times 10^{-14} - 1.6 \times 10^{-11}$	no data
Aldehydes	$\leq 6 \times 10^{-21}$	$1.0 - 3.1 \times 10^{-11}$	$0.3 - 2.0 \times 10^{-15}$
Ketones	$\leq 10^{-21}$	$2.1 \times 10^{-13} - 2.8 \times 10^{-11}$	no data
Amines	-	$2\text{-}10 \times 10^{-11}$	no data
Aromatics:			
Alkylbenzenes	$7 \times 10^{-23} - 2.2 \times 10^{-21}$	$0.2 - 6.2 \times 10^{-11}$	$\leq 1 \times 10^{-17} - 1.4 \times 10^{-16}$
Chloro, hydroxy and nitro aromatics	$\leq 4 \times 10^{-20} - 4.7 \times 10^{-19}$	$2.2 \times 10^{-13} - 6.7 \times 10^{-11}$	$5.0 \times 10^{-17} - 1.3 \times 10^{-11}$

class of organic compounds. Table 3.3-4 gives a ranking of the removal processes for two scenarios, one corresponding to the clean lower troposphere and the other to moderately polluted ambient air. It is evident from these two tables that only a few of the reactions listed are important for the removal of Level 2 contaminants in urban air. These reactions include reaction with OH for all categories; reaction with ozone for the more reactive unsaturated compounds; and, perhaps, reaction with NO_3 for the more reactive unsaturated aliphatics and polar aromatics. Our investigation of structure-reactivity relationships, which is described next, focused on these three subsets of reactions.

3.3.4 Structure-Reactivity Relationships

The basic underlying concept in structure-reactivity relationships (SRRs) is that, for a given reaction center, the rate of reaction with a given reactant is proportional to the electronic density at the reaction center. In other words, reaction rate constants correlate with those physical parameters that adequately describe the reaction center electronic density. In turn, such a correlation can be used to assess the validity of new experimental rate constant data, and to estimate the rate constants for structural homologues for which no data exist. SRRs have long been employed by physical organic chemists to elucidate reaction mechanisms (e.g. Taft, 1956; Hammett, 1970; Chapman and Shorter, 1972; Freeman, 1975; Exner, 1975). Their application to environmental chemistry considerations, although limited, is now receiving increasing attention (e.g. Grosjean et al., 1974; Grosjean, 1977; Radding et al., 1977; Gaffney and Levine, 1979; Mill, 1979; Wolfe et al., 1980; Gusten et al., 1981; Heicklen, 1981; Gusten et al., 1984; Dilling et al., 1985, 1986; Grosjean, 1986).

Let us start with a simple example. In the ozone-olefin reaction discussed earlier, the rate determining step is that of electrophilic addition of ozone to the unsaturated carbon-carbon bond. The rate of ozone attack will be a direct function of the nature and number of substituents attached to the reaction center. Thus, the rate constants for the reaction of ozone with methyl-substituted ethylenes increase with the number of methyl

Table 3.3-4

IMPORTANCE OF CHEMICAL REMOVAL PROCESSES FOR ATMOSPHERIC ORGANIC CONTAMINANTS

	Concentrations, molecules/cm^3					
	Scenario #1: "Clean" Lower Troposphere			Scenario #2: Moderately Polluted Urban Air		
Ozone	4.8×10^{11} (20 ppb)			2.4×10^{12} (0.1 ppm)		
OH (daytime)	1.0×10^{6} (0.04 ppt)			2.0×10^{6} (0.08 ppt)		
NO_3 (nighttime)	2.4×10^{8} (10 ppt)			1.2×10^{9} (50 ppt)		
Organics:	O_3	OH	NO_3	O_3	OH	NO_3
Unsaturated Aliphatics:						
Alkenes, dienes	Some	Major	Some?	Important	Important	Some?
Haloethenes	-	Major	-	Some?	Major	-
Saturated Aliphatics	Negligible	Major	Negligible	Negligible	Major	Negligible
Aromatics:						
Alkylbenzenes	Negligible	Major	Negligible	Negligible	Major	Negligible
Chloro, hydroxy and nitro aromatics	Negligible	Major	Some?	Negligible	Major	Some?

groups since CH_3 is an electron-donating group (positive inductive effect):

ethylene	$CH_2 = CH_2$	k = 1.0 (reference)
propene	$CH_2 = CHCH_3$	k = 7.9
cis 2-butene	$CH_3CH = CHCH_3$	k = 100
trimethyl ethylene	$(CH_3)_2C = CHCH_3$	k = 308
tetramethyl ethylene	$(CH_3)_2C = C(CH_3)_2$	k = 944

These rate constants are expected to correlate well with any parameter that describes the electronic density at the reaction center. One of these parameters (selected in this work for reasons discussed in more detail below) is the first ionization potential (IP), which is defined as the minimum energy required to ionize a molecule in the gas phase ($M + \text{energy} \rightarrow M^+ + e^-$). Indeed, such a correlation between ozone rate constants and IP exists, and is shown in Figure 3.3-1. Using the regression line, one can verify that the rate constant measured for cyclohexene is consistent with the value calculated using the IP of cyclohexene, 8.92 eV. One can also estimate the ozone reaction rate constant of 3-ethyl-2-pentene, $CH_3CH{=}C(C_2H_5)_2$, IP = 8.53 eV, for which no kinetic data exist. The rate constant thus estimated from the regression line in Figure 3.3-1 is 7.1×10^{-16} cm^3 $molecule^{-1}$ sec^{-1}.

3.3.5 The Use of Ionization Potentials in SRR

Several parameters have been used in SRR applications. These have included, besides ionization potentials, bond dissociation energies, polarity parameters such as the Taft and Hammet σ^* and σ^+, electron affinities, and functional group additivity increments (Heicklen, 1981; Atkinson and Aschmann, 1985; Atkinson, 1986a; Alfassi et al., 1986). We prefer to use ionization potentials for the following reasons:

- IPs are intrinsic and directly measurable properties of molecules. Other parameters such as σs or group increments are empirically derived from kinetic data, and reflect the uncertainties associated with these estimates. In addition, bond dissociation energies are not applicable in SRRs for electrophilic addition reactions, and also suffer from poor precision.

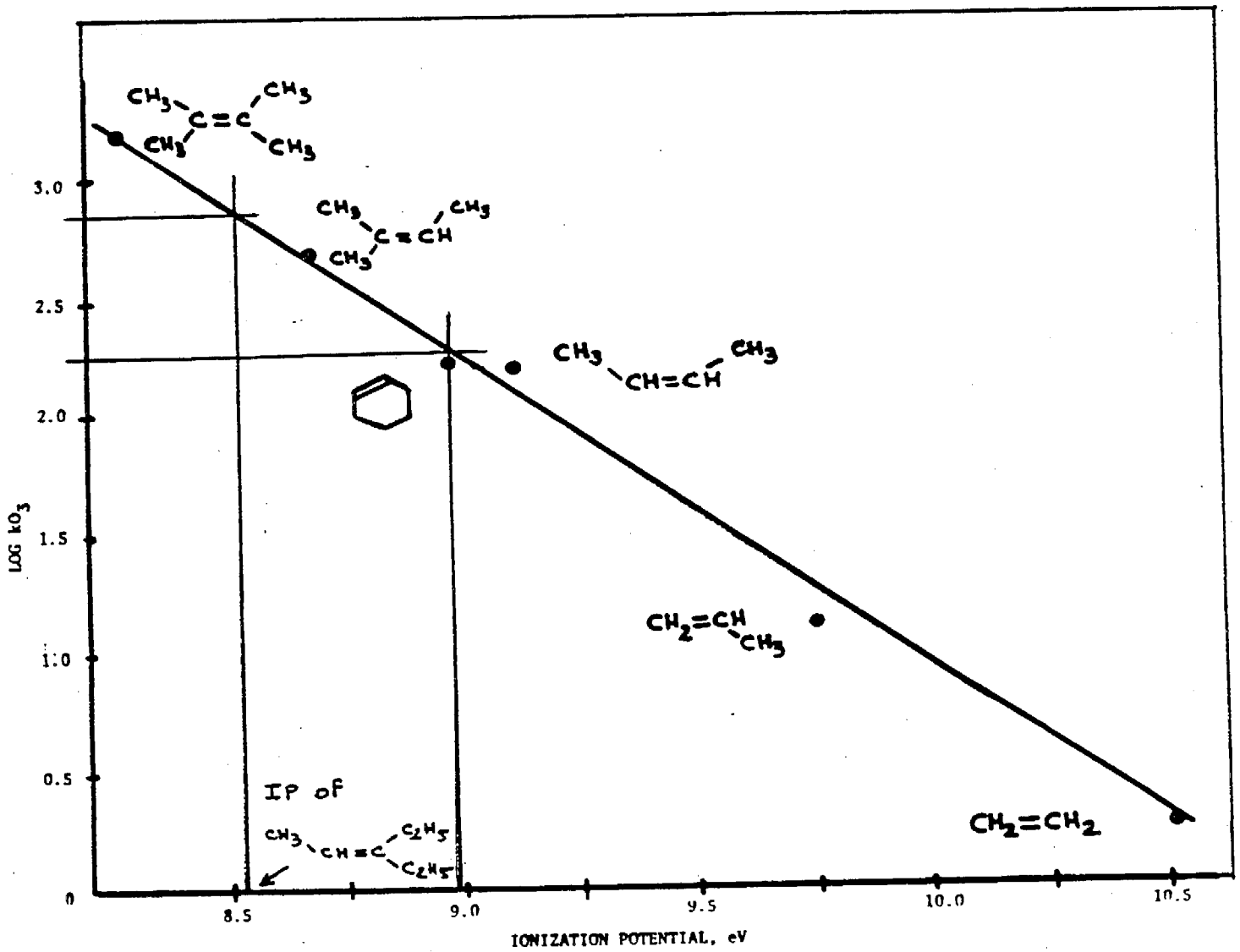


Figure 3.3-1. Example of Structure-Reactivity Relationship: Rate Constant for the Olefin-Ozone Reaction vs Olefin Ionization Potentials.

- IPs are available for hundreds of organic compounds. This is obviously a desirable feature when using SRRs to estimate rate constants.

- IPs are generally measured with excellent precision, with standard deviations of <0.05 eV. Values reported by different investigators rarely differ by more than 0.1 eV. Since IPs of most organics range from 7 to 13 eV, the precision on IP measurements is typically ≤ 1 percent. This is again a desirable feature for the predictive ability of SRRs. In contrast, reaction rate constants are typically reported with uncertainties of ± 20-30 percent, and results from different laboratories often differ by factors of two or more.

3.3.6 Critical Evaluation of Ionization Potentials and Reaction Rate Constants Data Sets

IPs were taken from the original references (Franklin et al., 1969; Cocksey et al., 1971; Watanabe et al., 1962; Staley et al., 1977; Aue et al., 1976; von Bischof and Heilbronner, 1970; Masclet et al., 1973; Carlier et al., 1974; Mouvier and Hernandez, 1975; Masclet and Mouvier, 1978) and supplemented by data from one compilation in the CRC Handbook of Chemistry and Physics. The Handbook data compilation was verified against the original references for most compounds.

All IPs were verified for consistency by constructing graphs of all individual values according to functional group, carbon number and degree of substitution. Examples of such plots are given in Figures 3.3-2, 3.3-3, and 3.3-4 for paraffins, amines and olefins, respectively. The IP trend for paraffins (Figure 3.3-2) is that of a monotonous decrease with substituent size. All alkyl groups have positive inductive effects (electron-donating), resulting in a decrease in IP from methane (CH_3R, R = H) to ethane (R = CH_3), from ethane to propane (R = C_2H_5), from propane to n-butane (R = n-C_3H_7) and isobutane (R = iso-C_3H_7), and so on. The incremental change in inductive effects decreases with increasing substituent size, and the IPs level off.

For functional groups allowing more than one degree of substitution at the reaction center, the IP will be most sensitive to the degree of substitution. This is shown in Figure 3.3-3 for amines, for which the IP decreases sharply from ammonia (NH_3, "zero" substitution) to primary (RNH_2),

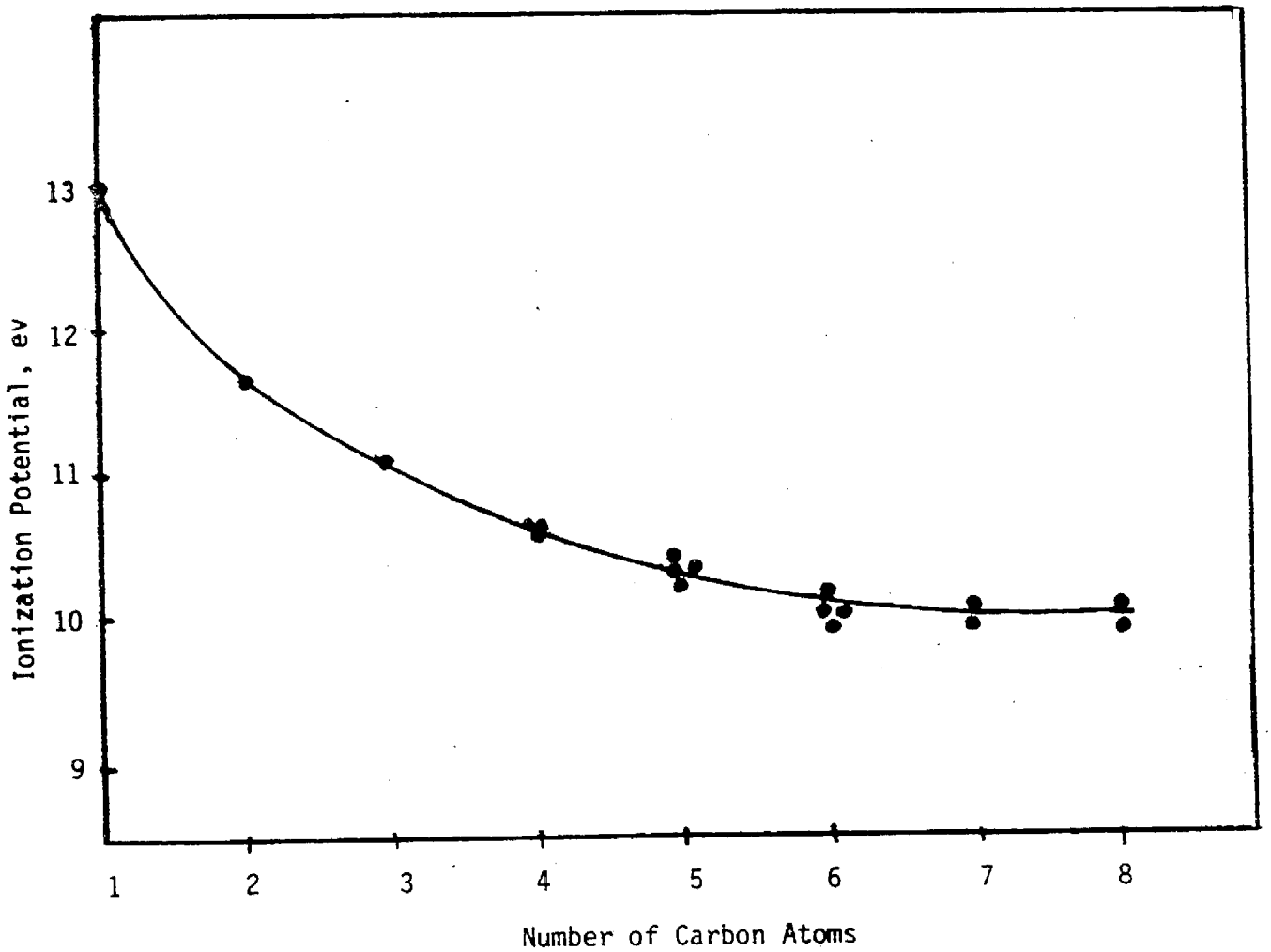


Figure 3.3-2. Effects of Substituents on the Ionization Potentials of Alkanes.

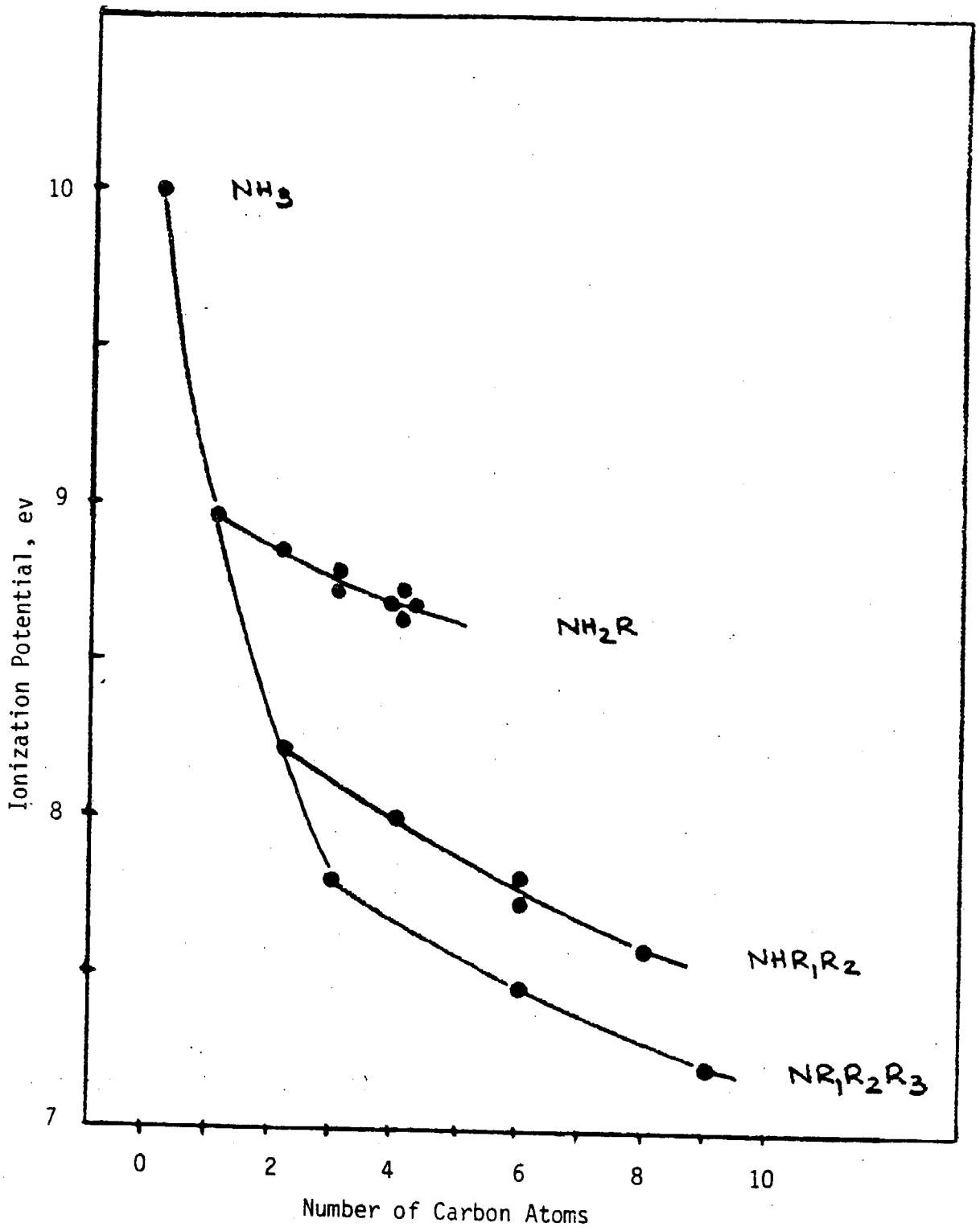


Figure 3.3-3. Effects of Substituents on the Ionization Potentials of Amines.

secondary (R_1R_2NH) and finally tertiary amines ($R_1R_2R_3N$). The same trend is seen for olefins (Figure 3.3-4) when replacing hydrogen atoms in the simplest member, ethylene ($CH_2=CH_2$) by one ($RCH=CH_2$), two (iso, $R_1R_2C=CH_2$, and cis and trans, $R_1CH=CHR_2$), three ($R_1R_2C=CHR_3$) and finally four alkyl groups ($R_1R_2C=CR_3R_4$). Within each degree of substitution is seen a secondary effect which is similar to that described above for paraffins, i.e. a decrease in IP with increasing substituent inductive effects. These plots also correctly describe several important structural effects on IPs, including the decreasing influence of the degree of substitution with increasing substitution (e.g. the interval between curves N_3 and N_2 is smaller than that between curves N_1 and N_2 in Figure 3.3-3, and the intervals in Figure 3.3-4 are $A_4-A_3 < A_3-A_2 < A_2-A_1$), and the relative stability of iso vs cis and trans disubstituted isomers (solid and dashed lines in Figure 3.3-4).

Because of the more limited data base, the evaluation of reaction rate constants could not be carried out with the same degree of detail as that for IPs. Consistency checks included, as for IPs, the analysis of trends in reactivity vs substituent effects for a given reaction (e.g. OH + olefins) or between reactions of the same type (e.g. OH addition to olefins vs O_3 addition to olefins). Rate constants already critically evaluated by panels of kineticists were used whenever available. These included the recommended CODATA and NASA-JPL rate constants for a number of OH-organic and Cl atom-organic reactions (Baulch et al., 1980; 1982; De More et al., 1985; Watson, 1977). Other rate constants were taken from the original peer-reviewed publications, with some bias towards the more recent references (Atkinson and Carter, 1984, and references therein for O_3 reactions; Atkinson, 1986b, and references therein for OH reactions; Atkinson et al., 1984a, 1984b, 1984c, 1985 and references therein for NO_3 reactions; Rinke and Zetzsch, 1983; Wahner and Zetsch, 1983; Becker et al., 1984; Ohta et al., 1986; Edney et al., 1986; Goodman et al., 1986; Davenport et al., 1986; Witte et al., 1986; Wallington et al., 1986). Absolute rate constants were preferred to relative rates derived from competitive measurements. Values from different laboratories, when substantially different, were not arbitrarily averaged. Rather, preference was given to those data sets that included compounds whose rate constants were internally consistent and were

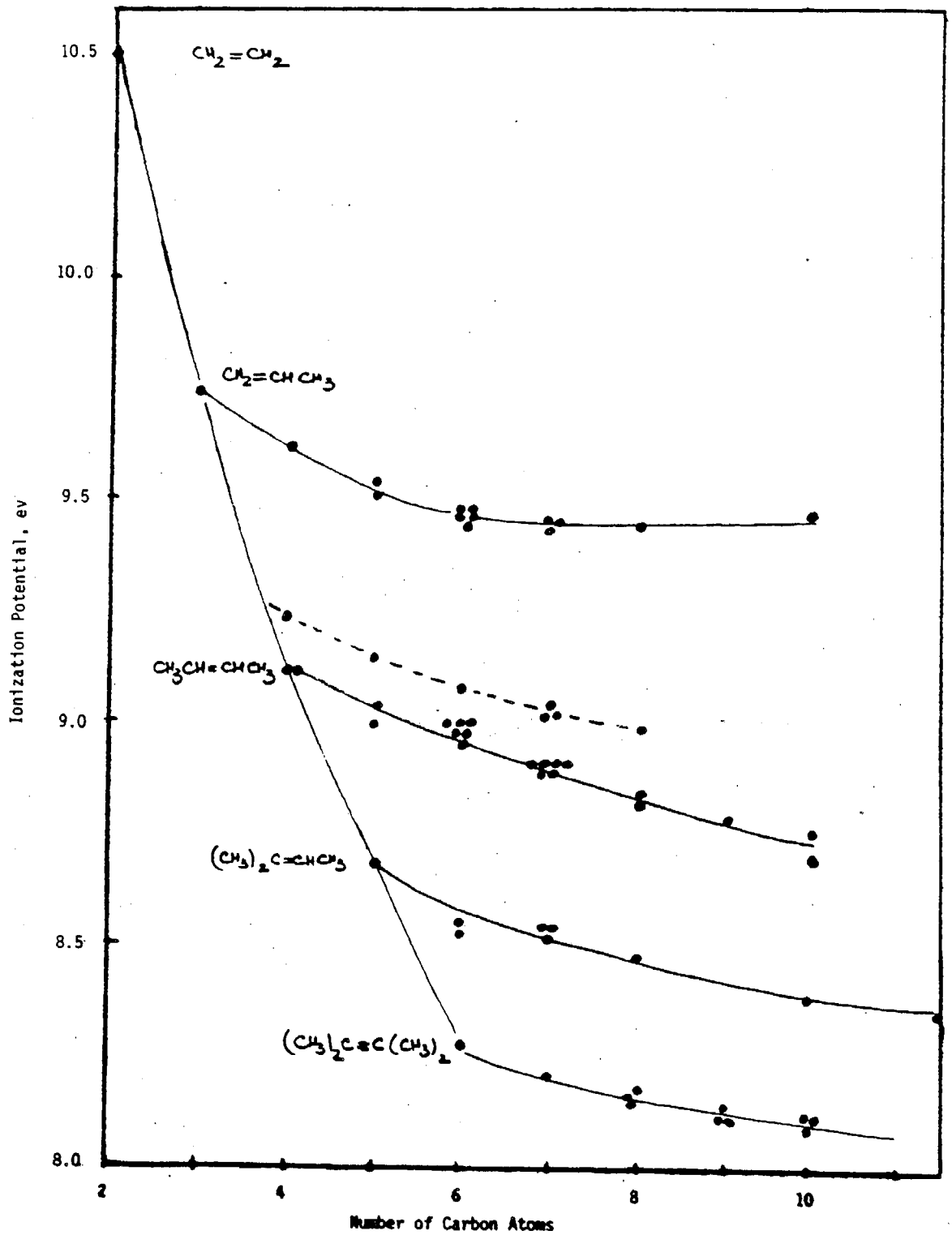


Figure 3.3-4. Effects of Substituents on the Ionization Potentials of Alkenes.

in good agreement with previous data. A number of rate constants could not be examined in a constructive way, and were simply used as reported.

3.3.7 SRR for Reactions with O_3, OH and NO_3

As mentioned before, reaction rate constants for O(3P), HO_2, NO_2 and chlorine atoms were reviewed, compiled, and employed for consistency checks of substitution effects, but are not included in our SRR analysis since the importance of these reactions is either negligible [HO_2, NO_2 and O(3P)] or undocumented (Cl atoms) in urban air. For the three reactions retained and involving ozone, OH and NO_3, again only those of importance in urban atmospheres were retained in the SRR analysis, and the others were employed for consistency checks of reactivity trends among electrophiles (e.g. ozone-aromatics vs OH-aromatics). Finally, classes of organics that do not include Level 2 contaminants (e.g. organosulfur compounds) or that were not necessary to estimate rate constants for Level 2 contaminants (e.g. haloalkanes and carbonyls), were also employed in trend and consistency checks but are not presented as SRR in this report.

The results are presented in Figures 3.3-5 (ozone-unsaturated aliphatics), 3.3-6 (nitrate radical-unsaturated aliphatics), 3.3-7 (hydroxyl radical-unsaturated aliphatics), 3.3-8 (hydroxyl radical-aromatics) and 3.3-9 (hydroxyl radical-saturated aliphatics). The corresponding slopes, intercepts and correlation coefficients are summarized in Table 3.3-5. Conclusions of a general nature are as follows:

- The expected trend of a decrease in reactivity with increasing IP was observed in all cases. These include three electrophiles (O_3, OH and NO_3), three types of reaction centers (saturated aliphatic, olefinic and aromatic) and two types of reactions, addition and abstraction (and both for aromatics, with addition being major at ambient temperature). These observations are consistent with theory for the electrophilic addition reactions. SRR involving IPs have seldom been examined for abstraction reactions. Keeping in mind that abstraction reactions may involve a rate-determining step, such SRR for electrophilic species is not inconsistent with theory.

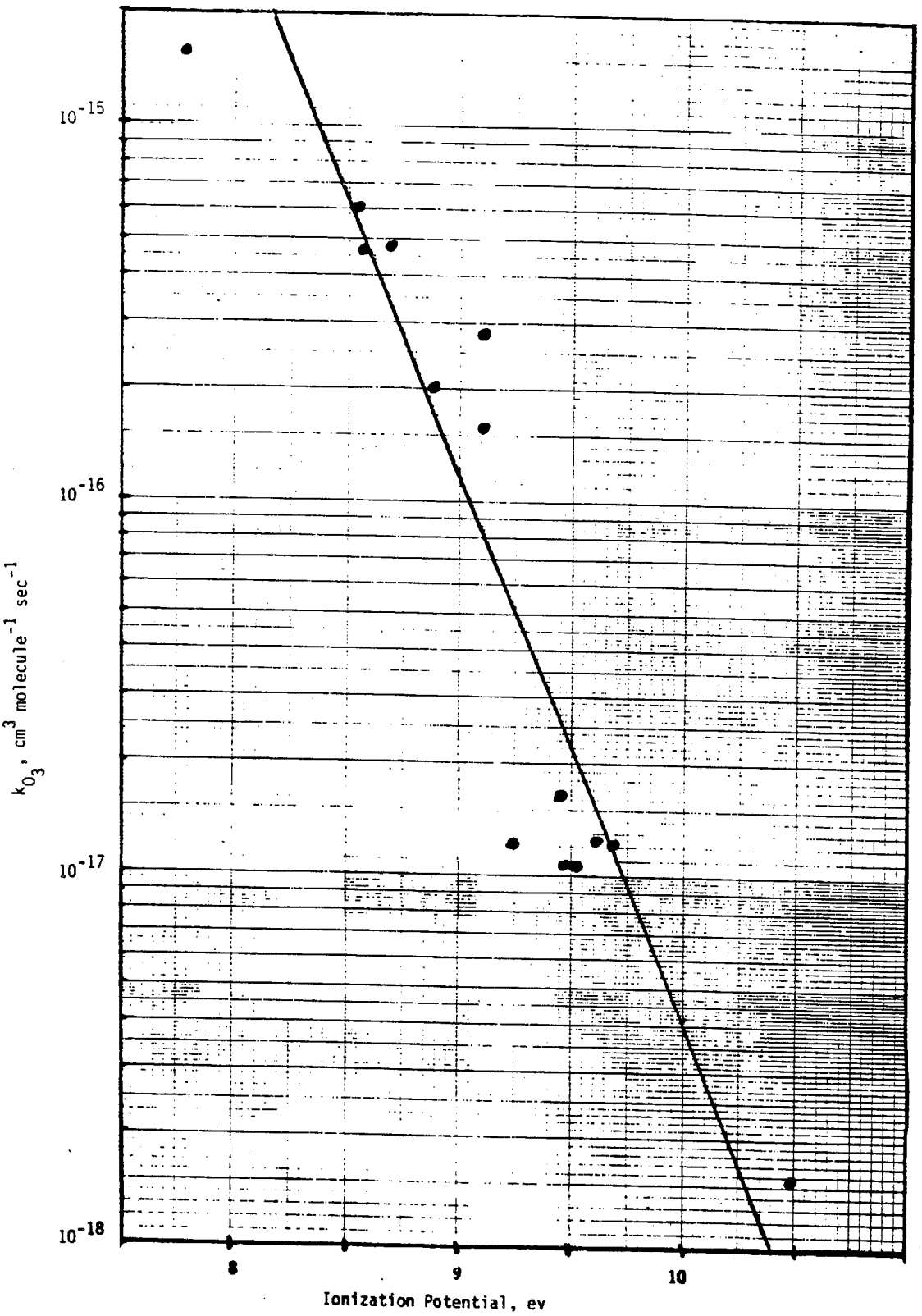


Figure 3.3-5. Structure-Reactivity Relationship for Ozone and Unsaturated Aliphatics.

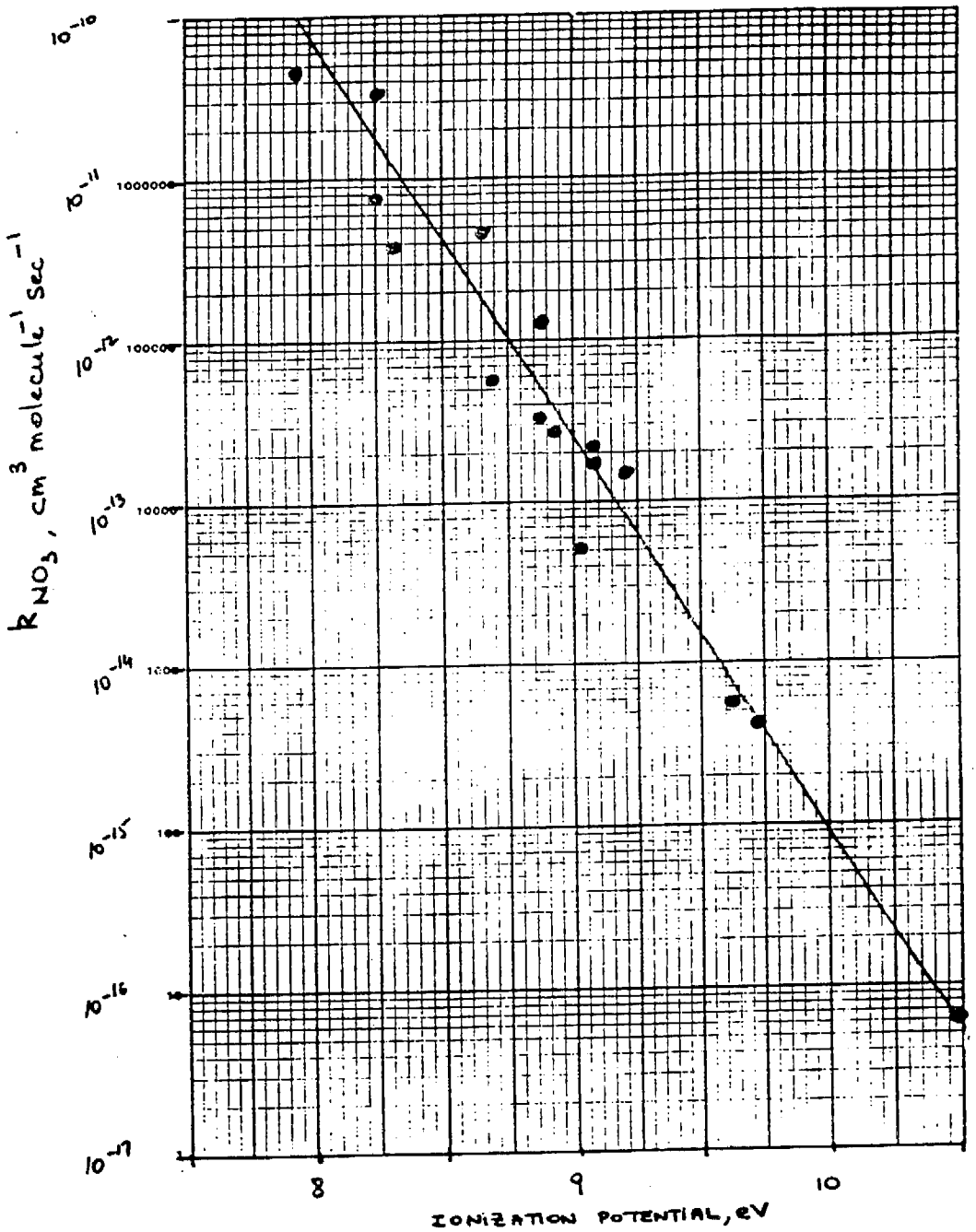


Figure 3.3-6. Structure-Reactivity Relationship for NO_3 and Unsaturated Aliphatics.

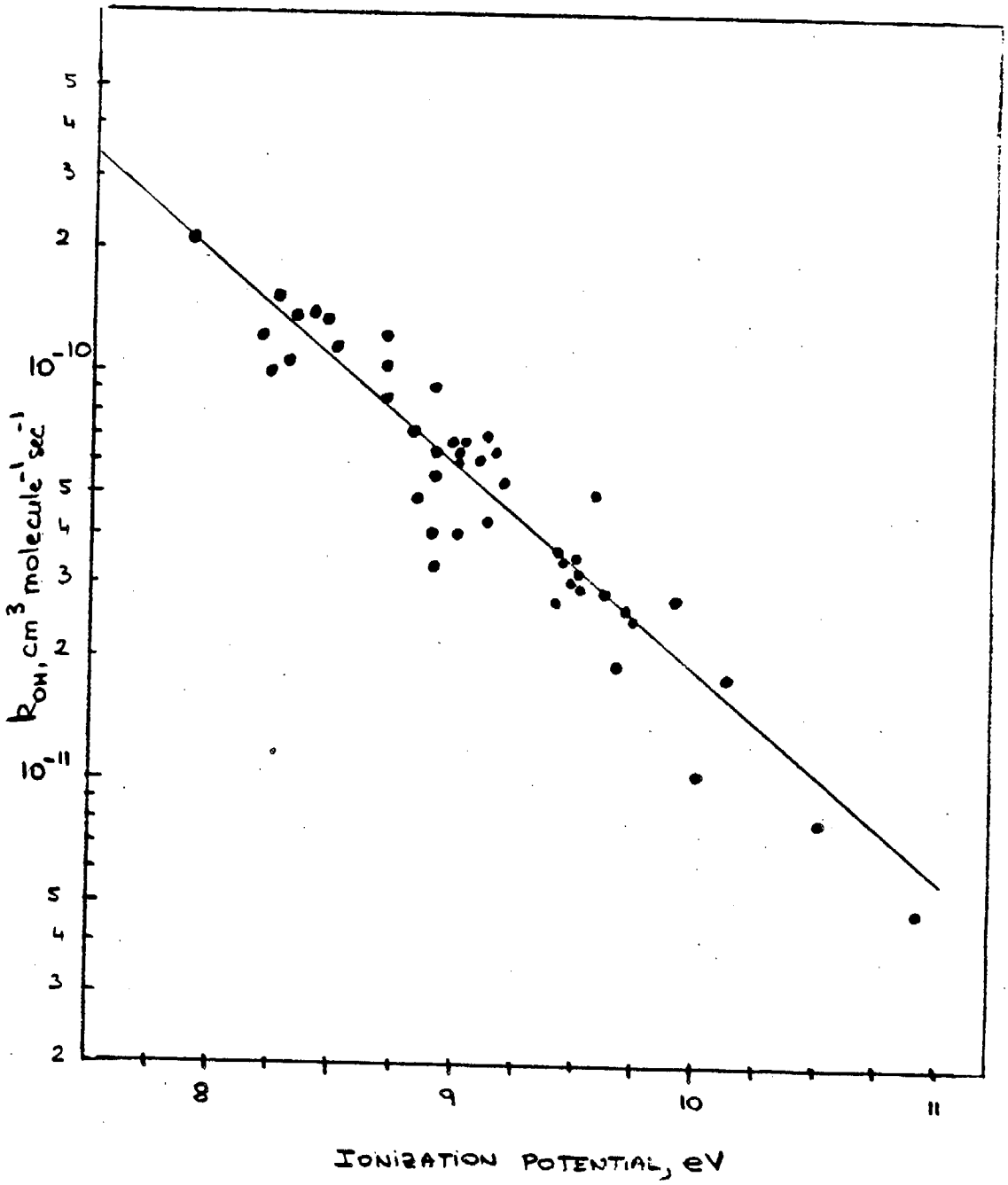


Figure 3.3-7. Structure-Reactivity Relationship for OH and Unsaturated Aliphatics.

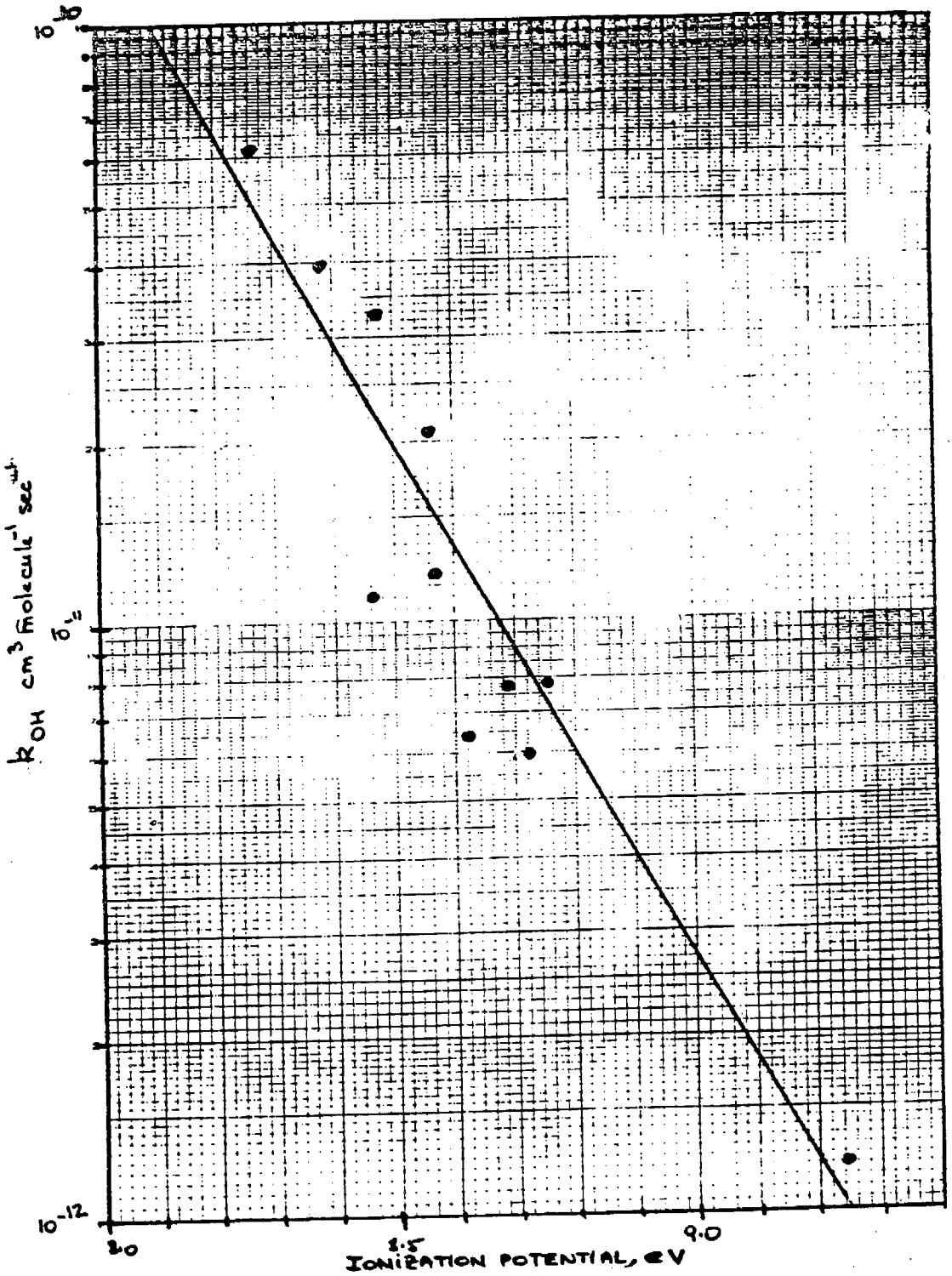


Figure 3.3-8. Structure-Reactivity Relationship for OH and Aromatics.

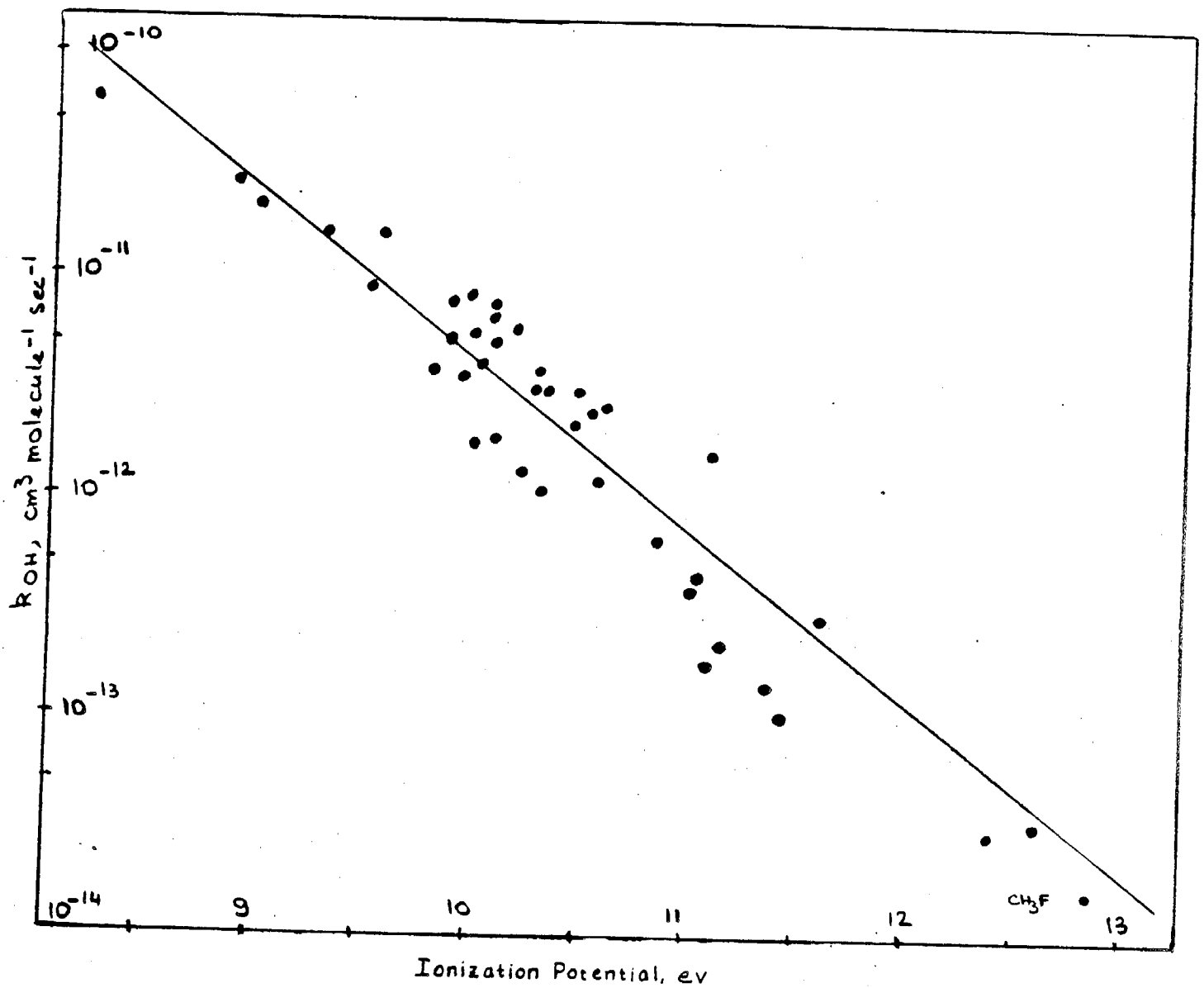


Figure 3.3-9. Structure-Reactivity Relationship for OH and Saturated Aliphatics.

Table 3.3-5

SLOPES, INTERCEPTS AND CORRELATION COEFFICIENTS OF LOG k VS IP RELATIONSHIPS

Reaction	Reaction Type	Slope	Intercept[a]	Correlation Coefficient	Number of Data Points
Ozone - olefins	Addition	-1.454	+15.16	0.941	14
NO_3 - olefins	Addition	-2.425	+24.26	0.973	15
OH - olefins	Addition[b]	-0.505	+5.31	0.941	45
OH - aromatics	Addition + Abstraction[c]	-1.730	+15.0	0.930	15
OH - saturated aliphatics	Abstraction	-0.779	+8.41	0.932	38

[a]Units: IP in electron volts in all cases; rate constants in $cm^3 molecule^{-1} sec^{-1} \times 10^{-18}$ (ozone-olefin), 10^{-15} (NO_3-olefin), 10^{-11} (OH-olefin and OH-aromatics) and 10^{-12} (OH-saturated aliphatics).

[b]May include a minor abstraction component for some compounds.

[c]Addition major at ambient temperature.

- All log k vs IP data sets could be reduced to linear expressions (Table 3.3-5), with reasonably good correlation coefficients of 0.930 to 0.973. While theory does not require reactivity and IP to be related in a linear fashion, such linear relationships have often been observed in the liquid phase (e.g. Grosjean et al., 1974; Freeman, 1975). We thus elected to use the straight lines, rather than some arbitrary curve-fitting expression, to estimate rate constants for Level 2 contaminants.

- The log k vs IP relationships shown in Figures 3.3-5 through 3.3-9 include compounds with a variety of functional groups. Thus, the unsaturated aliphatics included the alkenes, cyclic olefins, dienes, cyclodienes, unsaturated carbonyls and a number of difunctional unsaturated compounds. Saturated aliphatics included alkanes, cycloalkanes, alcohols, ethers, esters, amines, and a limited number of epoxides, nitriles, nitrate esters and carboxylic acids. We verified, for those subsets of compounds large enough to be statistically significant, that the relationship between log k and IP was consistent with the overall relation (Table 3.3-6). These observations confirm the validity of the SRR approach and increase our confidence in using SRR's to estimate unavailable rate constants for Level 2 contaminants and for many other potentially hazardous organics.

3.3.8 SRR-Estimated Rate Constants for Level 2 Contaminants

SRR-estimated rate constants are listed in Table 3.3-7 for each Level 2 contaminant and each type of reaction as appropriate. Rate constants for reaction with the hydroxyl radical were calculated for all Level 2 compounds. As discussed before, reactions with O_3 and NO_3 are of negligible atmospheric importance for saturated aliphatics, and the corresponding rate constants for saturated Level 2 aliphatics are not included in Table 3.3-7.

At this stage of our evaluation of Level 2 contaminants, the usefulness of the SRR approach becomes apparent. Of the 40 Level 2 compounds being reviewed, rate constants are available for only 11 organic-OH reactions, 10 organic-O_3 reactions (of which 9 are negligible for atmospheric removal) and 8 organic-NO_3 reactions (of which 3 are negligible), for a total of 29 reactions. Using measured IPs, which are available for 21 Level 2 compounds, rate constants could be estimated for 63 reactions. Using estimated IPs all of which could be estimated with reasonable precision (Table 3.3-8), rate constants could be estimated for 36 Level 2 compounds.

Table 3.3-6

LOG k VS IP RELATIONSHIP FOR SUBSETS OF ORGANIC COMPOUNDS

Reaction	Subset	Slope	Intercept[a]	Correlation Coefficient	Number of Data Points
OH - olefins	Alkenes only	-0.487	5.12	0.936	24
	Alkenes + dienes	-0.514	5.41	0.942	36
	(overall)	(-0.505)	(5.31)	(0.941)	(45)
OH - saturated aliphatics	Alkanes only	-0.875	9.57	0.956	16
	+ alcohols	-0.888	9.70	0.953	21
	+ ethers	-0.841	9.17	0.951	25
	+ esters	-0.816	8.85	0.887	29
	(overall)	(-0.779)	(8.41)	(0.932)	(38)
NO_3 - olefins	Alkenes only	-2.617	26.16	0.992	9
	Dienes only	-2.494	24.39	0.984	4
	(overall)	(-2.425)	24.26	0.973	15

[a]Same units as in Table 3.3-5.

Table 3.3-7

RATE CONSTANTS ESTIMATED FROM STRUCTURE-REACTIVITY RELATIONSHIPS

(Units: $cm^3 molecule^{-1} sec^{-1}$)

Level 2 Compound	IP (eV)	k_{OH} Estimated	k_{OH} Literature	k_{O_3} Estimated	k_{O_3} Literature	k_{NO_3} Estimated	k_{NO_3} Literature
Acetaldehyde	10.22	-[a]	1.2×10^{-11}	negligible	$<6 \times 10^{-21}$	-[a]	1.3×10^{-15}
Acrolein	10.11	1.6×10^{-11}	1.8×10^{-11}	2.8×10^{-18}	2.8×10^{-19}	5.5×10^{-16}	no data
Acrylonitrile	10.91	6.3×10^{-12}	4.9×10^{-12}	1.9×10^{-19}	$<1.0 \times 10^{-19}$	6.3×10^{-18}	no data
Allyl chloride	10.04	1.7×10^{-11}	no data	3.6×10^{-18}	no data	8.2×10^{-16}	no data
Benzyl chloride	9.19	1.3×10^{-12}	no data	negligible	$<4 \times 10^{-20}$	negligible	no data
<u>Chlorobenzenes</u>							
Chlorobenzene	9.07	2.0×10^{-12}	no data	negligible	no data	negligible	no data
p-dichlorobenzene	8.95	3.3×10^{-12}	no data	negligible	no data	negligible	no data
trichlorobenzene	9.10	1.8×10^{-12}	no data	negligible	no data	negligible	no data
hexachlorobenzene	9.15	1.5×10^{-12}	no data	negligible	no data	negligible	no data
Chloroprene	8.95	6.2×10^{-11}	no data	1.4×10^{-16}	no data	3.6×10^{-13}	no data
<u>Cresols</u>							
o-cresol	8.52	1.8×10^{-11}	4.7×10^{-11}	negligible	2.5×10^{-19}	-[d]	1.2×10^{-11}
m-cresol	8.52	1.8×10^{-11}	6.7×10^{-11}	negligible	1.9×10^{-19}	-[d]	9.2×10^{-12}
p-cresol	8.42	2.7×10^{-11}	5.2×10^{-11}	negligible	4.7×10^{-19}	-[d]	1.3×10^{-11}
<u>Dialkylnitrosamines</u>[b]							
dimethyl	8.24-9.5	$(1\text{-}9 \times 10^{-11})$	no data	negligible	no data	negligible	no data
diethyl	8.01-9.5	$(1\text{-}14 \times 10^{-11})$	no data	negligible	no data	negligible	no data
methylethyl	9.12-9.5	$(1\text{-}12 \times 10^{-11})$	no data	negligible	no data	negligible	no data
1,4-dioxane	9.13	2.0×10^{-11}	no data	negligible	no data	negligible	no data

Table 3.3-7 (Continued)

RATE CONSTANTS ESTIMATED FROM STRUCTURE-REACTIVITY RELATIONSHIPS

(Units: $cm^3 molecule^{-1} sec^{-1}$)

Level 2 Compound	IP (eV)	k_{OH} Estimated	k_{OH} Literature	k_{O_3} Estimated	k_{O_3} Literature	k_{NO_3} Estimated	k_{NO_3} Literature
Epichlorohydrin	10.08	3.6×10^{-12}	no data	negligible	no data	negligible	no data
<u>Ethylene glycol ethers</u>							
Monomethyl	9.43	1.1×10^{-11}	no data	negligible	no data	negligible	no data
Monoethyl	9.23	1.6×10^{-11}	no data	negligible	no data	negligible	no data
Monobutyl	9.08	2.1×10^{-11}	no data	negligible	no data	negligible	no data
Hexachlorocyclopentadiene	8.60	9.3×10^{-11}	no data	4.5×10^{-16}	no data	2.5×10^{-12}	no data
Maleic anhydride	9.26	4.3×10^{-11}	no data	4.9×10^{-17}	no data	6.4×10^{-14}	no data
Manganese, $C_5H_5Mn(CO)_3$	8.30	$0.9\text{-}1.3 \times 10^{-10}$ [c]	no data	negligible	no data	negligible	no data
Methyl bromide	10.53	- [e]	3.5×10^{-14}	negligible	no data	negligible	no data
Mercury, dimethyl	9.00	2.5×10^{-11}	no data	negligible	no data	negligible	no data
Nitrobenzene	9.92	6.9×10^{-14}	no data	negligible	no data	negligible	no data
Nitrosomopholine [b]	8.0-9.5	$(1\text{-}15 \times 10^{-11})$	no data	negligible	no data	negligible	no data
<u>Phenols</u>							
Phenol	8.50	2.0×10^{-11}	no data	negligible	no data	- [d]	2.1×10^{-12}
2-nitrophenol	9.62	2.3×10^{-13}	no data	negligible	no data	negligible	no data
4-nitrophenol	9.52	3.4×10^{-13}	no data	negligible	no data	negligible	no data
3-nitro-o-cresol	9.62	2.3×10^{-13}	no data	negligible	no data	negligible	no data

Table 3.3-7 (Continued)

RATE CONSTANTS ESTIMATED FROM STRUCTURE-REACTIVITY RELATIONSHIPS

(Units: $cm^3 molecule^{-1} sec^{-1}$)

Level 2 Compound	IP (eV)	k_{OH} Estimated	k_{OH} Literature	k_{O_3} Estimated	k_{O_3} Literature	k_{NO_3} Estimated	k_{NO_3} Literature
5-nitro-o-cresol	9.52	3.4×10^{-13}	no data	negligible	no data	negligible	no data
2,4-dinitro-o-cresol	10.13	3.0×10^{-14}	no data	negligible	no data	negligible	no data
Phosgene	11.77	$<1.7 \times 10^{-14}$	no data	negligible	no data	negligible	no data
Propylene oxide	10.22	2.8×10^{-12}	1.3×10^{-12}	negligible	no data	negligible	no data
Vinylidene chloride	9.70	2.6×10^{-11}	no data	negligible	3.7×10^{-21}	5.5×10^{-15}	no data
o-xylene	8.57	1.5×10^{-11}	1.2×10^{-11}	negligible	7.0×10^{-22}	negligible	1.1×10^{-16}
m-xylene	8.57	1.5×10^{-11}	2.1×10^{-11}	negligible	6.0×10^{-22}	negligible	7.6×10^{-17}
p-xylene	8.46	2.3×10^{-11}	1.1×10^{-11}	negligible	no data	negligible	1.4×10^{-16}

[a]Only aldehyde in Level 2 list, hence no SRR was needed for this category.

[b]Large uncertainty in IP and log k_{OH} for nitrosamines, but not critical since photolysis is major removal process.

[c]Mechanism unknown; possibly addition on cyclopentadiene unsaturated bond. Estimated rate is fast, i.e. reaction occurs every third collision.

[d]No SRR can be constructed for NO_3 + phenols (IP data available for only 4 phenols, all four have same IP). The reaction of NO_3 with nitrophenols is estimated to be slow, i.e. $k = 1.0 \times 10^{-14} cm^3 molecule^{-1} sec^{-1}$.

[e]Only haloalkane in Level 2 list, hence no SRR was needed for this category.

Table 3.3-8

ESTIMATED IONIZATION POTENTIALS

Compound	Estimated Value (eV)	Method
Vinylidene chloride	9.70 ± 0.005	From curves of IP vs number of substituents for methyl and chloro substituted ethylenes, also taking into account the iso vs cis (or trans) effect for isomers.
Maleic anhydride	9.26 ± 0.07	Comparison of cis-2-butene and vinyl acetate.
Chloroprene	8.95 ± 0.05	From butadiene, isoprene, and chlorinated alkenes.
Epichlorohydrin	10.08 ± 0.14	From propane, epoxypropane, and n-propyl chloride.
Ethylene glycols		
methyl ether	9.43 ± 0.27	From IP vs substituent size for ethers, and replacing $-CH_2CH_3$ by $-CH_2CH_2OH$.
ethyl ether	9.23 ∓ 0.27	
butyl ether	9.08 ∓ 0.27	
Hexachlorocyclopentadiene	8.60 ± 0.3	From cyclopentadiene, effect of chlorine atoms in diolefins, offset by the opposite effect of the chlorine atoms on the single saturated carbon atom.
Trichlorobenzene	9.10 ± 0.10	From benzene, chlorobenzene, dichlorobenzene isomers, and hexachlorobenzene.
Ortho cresol	8.52 ± 0.10	Same as meta cresol; ortho and meta hydroxy and chloroaromatics have same IP, para isomer is 0.10 ± 0.02 eV lower.
Para cresol	8.42 ± 0.10	See ortho cresol.
2-nitrophenol	9.62 ± 0.05	From 4-nitrophenol.
3-nitro-o-cresol	9.62 ± 0.10	Same as nitrophenol.
5-nitro-o-cresol	9.52 ± 0.10	See 3-nitro-o-cresol.
2,4-dinitro-o-cresol	10.13 ± 0.51	Upper limit is estimated by assuming additive effect of ortho-nitro and para-nitro group; lower limit is IP of 3-nitro-o-cresol.
Nitrosamines		
dimethyl	8.24 - 9.5	No data: lower limit is IP of amine, higher limit is consistent with Meili et al. (1979), who observed no response for dimethyl and diethyl nitrosamine with a 9.5-eV lamp photoionization detector.
methyl-ethyl	8.12 - 9.5	
diethyl	8.01 - 9.5	
nitrosomorpholine	8.0 - 9.5	

The four remaining Level 2 compounds are the nitrosamines, for which only rough estimates of the IPs could be made. Other sources of data that could be exploited in SRR were examined. Rate constants for gas phase reactions with other species, which could be exploited in a log k (X) - log k (OH) plot, are available for a number of organics but not nitrosamines. Rate constants for liquid phase reactions of OH with organics, which could be exploited with a log k_{OH} (gas phase) vs log k_{OH} (liquid phase) plot (e.g. Güsten et al., 1981; Dilling et al., 1985), were also examined. The data base for OH reactions in the liquid phase, while including many organics (but only one Level 2 compound) does not contain data for nitrosamines. We also elected not to use the estimated values that can be found in several reports for the OH reaction (e.g. Radding et al., 1977; Cupitt, 1980) since these estimates, although possibly reasonable, were not documented. However, this failure to obtain good estimates for the reaction of nitrosamines with OH, O_3 and NO_3 is not critical: nitrosamines photolyze rapidly in sunlight:

$$R_2NNO + h\nu \rightarrow R_2\dot{N} + NO$$

with half-lives of 30 to 60 minutes (Hanst et al., 1977). Other reactions of nitrosamines in the atmosphere, for which no reliable estimates could be derived from SRR analysis, are slow compared to their removal by photolysis.

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