4.0
EVALUATION OF ACETALDEHYDE

4.1 PHYSICAL AND CHEMICAL PROPERTIES

Acetaldehyde is a volatile colorless liquid. Table 4.1-1 summarizes some of its physical and chemical properties.

4.2 DIRECT PRODUCTION IN CALIFORNIA

There are only two U.S. manufacturers of this compound. Neither manufacturer makes or uses acetaldehyde in California (Doerr, 1985; Johann, 1985; Stafford, 1985; Stehr, 1985).

4.3 INDIRECT PRODUCTION AND EMISSIONS IN CALIFORNIA

Acetaldehyde is emitted to the atmosphere through a variety of combustion sources, including motor vehicles, aircraft, fossil-fueled power plants, industrial and domestic furnaces, wood-burning stoves and fireplaces, coffee roasting, and tobacco smoke.

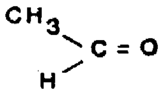
4.3.1 Mobile Sources

4.3.1.1 Emission Factors Background

Although acetaldehyde may be emitted from various mobile sources, including on-road passenger vehicles, trucks, aircraft, and boats, our analysis has focused on light duty passenger vehicles and trucks, for which sufficient aldehyde speciation data exist. Since the mid-1970s a number of studies of aldehyde emissions, from a variety of types of vehicles, have been conducted. The most common focus has been on the dominant emission component, formaldehyde. However, sufficient data have been collected on acetaldehyde, in automobiles equipped with catalysts and in those without catalysts, and on light and heavy duty trucks, to obtain an understanding of the approximate magnitude of emissions from such vehicles (Baines et al., 1982; Black et al., 1984; Carey, 1981; Gabele et al., 1977; Nebel, 1981; Sigsby et al., 1984; Smith, 1983; Smith and Urban 1982).

Table 4.1-1

CHEMICAL DATA SUMMARY FOR ACETALDEHYDE

Property	Value for Acetaldehyde
CAS Registry No.	75-07-0
Synonyms	Acetic aldehyde, ethyl aldehyde, ethanal
Molecular Weight	44.05
Molecular Formula	C_2H_4O
Molecular Structure	
Physical State at STP	Volatile colorless liquid
Boiling Point	20.8°C at 760 mm
Melting Point	-121°C
Specific Gravity	0.7834 at 18°C/4°C
Vapor Pressure	923 torrs at 25°C
Vapor Density (air = 1)	1.52
Solubility	Infinite (Hot H_2O)
Log Partition Coefficient (octanol/H_2O)	0.43
Henry's Law Constant	

Source: SAI (1980), Sittig (1981), and Verschueren (1977).

Emissions From Light Duty Vehicles

Non-catalyst-equipped cars from the early 1970s, or prior model years, had approximate total aldehyde emission rates ranging from 12 to 200 mg/km, with an average of approximately 85 mg/km (Carey, 1981; Nebel, 1981; Sigsby et al., 1984; Smith, 1983). Most early mobile source emission studies did not isolate individual aldehyde species. Recent studies with catalyst equipped vehicles have indicated that acetaldehyde emissions ranged from 9.9 to 25 percent of total aldehyde emissions (Sigsby et al., 1984). It would be convenient to use these figures to obtain approximate values for non-catalyst automobiles. However, catalyst-equipped vehicle data cannot readily be applied to pre-catalyst automobiles, because acetaldehyde's fraction of total aldehyde emissions is quite variable (Carey, 1981; Gabele et al., 1977; Sigsby et al., 1984).

Total aldehyde emissions from catalyst-equipped light duty vehicles are approximately 1/20 those of non-catalyst-equipped vehicles. Studies several years ago indicated that typical total aldehyde emission rates for catalyst-equipped automobiles average around 2.5 mg/km, although particular vehicles may have emissions as high as 6 to 7 mg/km. Typical acetaldehyde emissions found in three EPA-sponsored studies were 0.25 mg/km (Carey, 1981). These emission factors are reported in Table 4.3-1 along with emission factors for various types of trucks. Three-way catalyst-equipped vehicles have the lowest aldehydes emissions, while oxidation catalysts tend to produce somewhat higher emissions.

Sigsby et al. (1984), in a recent draft paper prepared for the EPA, report acetaldehyde emissions from 46 light duty vehicles which were in-use loaners from the public. These vehicles were chosen to approximate the actual passenger vehicle mix in the U.S.; model years ranged from 1975 to 1982. Emission factors calculated for these automobiles, therefore, may be more appropriate for on-road light duty vehicles. This study used a larger sample than did those reported earlier; for example, the emission factors from several light duty vehicle studies reported by Carey (1981) were based upon 13 vehicles, only some of which had 3-way catalysts.

Table 4.3-1

PRE-1981 VEHICLE EMISSION FACTORS FOR ACETALDEHYDE

Vehicle Category	Typical Emission Factor (mg/km)	Upper-Bound Emission Factor (mg/km)	Comments
Light duty passenger vehicles (with catalytic converter)	0.25	0.40	
Light duty trucks	-	-	These vehicles have not been tested. The same emission factors used for passenger vehicles will be used for this category.
Medium duty trucks	4.22	10.50	Emission factors for vehicles in this category are approximated by those found for light duty diesels.
Heavy duty trucks	19.40	37.40	This category combines gasoline and diesel powered vehicles to increase sample size.

Source: Carey, 1981

Three test procedures were used with the vehicles in the Sigsby et al. study: the Federal Test Procedure driving cycle (FTP), the New York City driving cycle (NYCC), and the Crowded Urban Expressway driving cycle (CUE). Each test simulates a different type of driving environment. The FTP, which has been the most frequently used procedure for studies of this type, uses the Urban Dynamometer Driving Schedule for its testing protocol. This schedule, in turn, has a transient phase with hot and cold starts, and a cold start stabilized phase, simulating a typical urban driving pattern as would have been seen in Los Angeles in the late 1960s. The NYCC is a low speed driving cycle, similar to crowded central city driving conditions. The CUE represents normal high speed driving. Emission factors for the 46 light duty vehicles are reported in Table 4.3-2.

Emissions From Trucks

Emissions from light and heavy duty gasoline and diesel trucks have also been the subject of several studies (Carey, 1981; Black and High, 1984). Carey summarized findings indicating that total aldehyde emissions from light duty diesels varied between 8.75 and 76.5 mg/km, with an average of 36.7 mg/km, in two EPA-sponsored studies. The average acetaldehyde emissions were 4.22 mg/km. One study performed for the EPA reported that heavy duty vehicles emitted an average of 19.4 mg/km of acetaldehyde and 140 mg/km of total aldehydes (Carey, 1981).

Warner-Selph and Dietzmann (1984) have recently published a paper, sponsored by the EPA, which discusses emission tests on 5 buses and 19 heavy-duty diesel trucks, all with accumulated mileage between 33,000 and 266,000 miles. The vehicles were tested using the Recommended Practice for Determining Exhaust Emissions from Heavy-Duty Vehicles Under Transient Conditions. In view of the small fraction of total vehicle miles driven by buses, they are likely to contribute relatively little to California emissions. Therefore, we disregard bus emissions in our acetaldehyde emission calculations. The mean acetaldehyde emissions for the remaining 19 vehicles was 62.9 mg/km. Using two standard deviations above the mean as a rough measure, we obtain 189.1 mg/km for the upper bound estimate of emissions per vehicle. These emission factors are reported in Table 4.3-3.

Table 4.3-2

EMISSION FACTORS FOR ACETALDEHYDE FOR LIGHT DUTY VEHICLES[a]

	NYCC	FTP	CUE
Total Aldehydes (mg/km)	70.810	26.580	18.490
Acetaldehyde's Percent by Weight of Total Aldehydes (% of total)	24.031	25.190	27.903
Standard Deviation (mg/km)	8.797	2.310	2.925
Mean Acetaldehyde (mg/km)	17.016	6.696	5.159
Upper Bound Acetaldehyde ($\overline{X}+2\sigma$) (mg/km)	34.611	11.316	11.010

[a] Calculations by SAIC from data by Sigsby et al., 1984.

Table 4.3-3

EMISSION FACTORS FOR ACETALDEHYDE FOR HEAVY DUTY TRACTOR-TRUCKS[a]

Category	Emission Factor (mg/km)
Typical ($\overline{X}$)	62.9
Standard Deviation (σ)	63.1
Upper Bound ($\overline{X} + 2\sigma$)	189.1

[a] Calculations by SAIC from data reported by Warner-Selph and Dietzmann, 1984. Sample size equals 19 trucks.

Emissions Under Non-Standard Conditions

With the exception of the two recent EPA-sponsored studies on light duty vehicles and heavy duty tractor-trucks and buses, most of the above results were obtained with production vehicles which were fairly new and had been tuned to manufacturers' specifications. Inasmuch as the majority of vehicles only approximated these conditions, several studies focused on other variables that might affect aldehyde emissions, including the effects of mileage, misfueling, alternative fuel mixtures, and a variety of malfunction conditions.

Carey (1981) reported the results of one study of aldehyde emissions in catalyst-equipped vehicles during a 15,000 mile run. Acetaldehyde emissions increased by a factor of 2 to 4 during the test. Nebel (1981) reported that misfueling (placing leaded gasoline in the fuel tank of an automobile equipped with a catalytic converter) increased emissions of aldehydes rather rapidly as mileage accumulated. Switching back to unleaded gasoline, after driving for 5,000 miles with leaded fuel, reduced aldehyde emissions slightly, but they still remained considerably above baseline levels. This suggested a slight rejuvenation of the catalyst (Nebel, 1981). Even after 5,000 miles on leaded gasoline, catalyst-equipped vehicles had aldehyde emissions only one third to one half those of non-catalyst equipped cars.

Emissions were examined for a variety of malfunctioning engine and emission control device conditions, including misfiring and rich and lean idle configurations. Although results were quite variable, the general trend was toward increased acetaldehyde and total aldehyde emissions. Maximum emissions of aldehydes appeared to occur at 12 degrees misfire, at which point acetaldehyde emissions increased from 6 to 15 times over baseline (Carey, 1981; Urban, 1981).

Finally, the effect of several varieties of alternative gasoline fuel mixtures on emissions has been examined (Smith, 1983). These results appeared to indicate that the very low emission rates of acetaldehyde and total aldehydes characteristic of modern three-way catalytic converters were not affected by a fuel mixture of gasoline and naphtha or gasoline and methanol. In one test of a fuel injected 1981 Volkswagen Rabbit equipped with a three-way catalytic converter, acetaldehyde emissions for five mixtures of alternative fuels with gasoline were below the measurement threshold and reported as 0 mg/km.

4.3.1.2 Emissions from Mobile Sources in California

Automobiles and Trucks

Mobile sources are divided by the ARB into the following categories: light duty automobiles, light duty trucks, medium duty trucks, heavy duty gasoline trucks, heavy duty diesel trucks, and motorcycles. Table 4.3-4 shows the 1985 California mileage for each vehicle classification, determined by the California Air Resources Board (Avlani, 1986).

A literature search revealed that acetaldehyde emission factors have been calculated only for light duty passenger vehicles, light duty diesel vehicles, and heavy duty trucks. Considerably more research has been done on recent models of light duty passenger vehicles than on vehicles in the other categories. Even so, most research has only indirectly been concerned with aldehydes other than formaldehyde. Our estimates of emissions will be relatively crude approximations because of the following:

- Variation among vehicles;
- Different catalytic systems, in the various models, with a variety of efficiencies in removing aldehydes;
- Relatively few vehicles tested in some vehicle categories and lack of representativeness of tested vehicles in all categories;
- The necessity of combining categories and approximating emission factors for vehicle categories that have been insufficiently tested;
- Increasing aldehyde emissions with vehicle mileage; and

Table 4.3-4

VEHICLE MILES TRAVELLED IN CALIFORNIA IN 1985[a] (millions)

Vehicle Classification	Vehicle Miles Travelled
Automobiles	124,730
Light duty trucks	24,474
Medium duty trucks	7,224
Heavy duty trucks	13,139

Source: California Air Resources Board (Avlani, 1986).

[a] Excludes motorcyles.

- Increasing aldehyde emissions with a variety of potential engine malfunctions.

For the present study, we use two sets of data to make two estimates of acetaldehyde emissions in the state. The first set of emission factors are found in the literature prior to 1981 (Carey, 1981) and were reported in Table 4.3-1. The second column reports mean or typical emission factors, while the third indicates the likely upper bound of emission factors corresponding to the vehicles tested. The second set of emission factors are based upon two recent EPA studies and are listed in Tables 4.3-2 and 4.3-3.

Emissions Based on Pre-1981 Data. Most light duty vehicles in earlier studies were low mileage automobiles, adjusted to manufacturers' specifications before testing. Emission tests for aldehydes at higher mileage indicated that aldehyde emissions increased by two to four times as mileage increased. In our estimates for light duty vehicles, we assume that the actual on-road vehicle mileage varies considerably. To account conservatively for the mileage on operating automobiles, we multiply emission factors by an adjustment factor of two for a "typical" passenger vehicle and by a factor of three for the upper bound estimate. We also use these adjustment factors for light and medium duty trucks, but not for heavy duty trucks, since emission factors for trucks were initially calculated for high mileage vehicles.

A second adjustment factor is required to take possible engine malfunctioning into account. A variety of engine malfunction conditions were examined for their effect on aldehyde emissions. In most cases malfunctioning led to increased emissions. As mentioned previously, the maximum increase occurred in a mistuned engine with a 12 degree misfire condition. In this case, aldehyde emissions increased from 6 to 15 times baseline levels. A certain percent of vehicles on the road are out of tune or have one or more of a variety of engine malfunctions. The exact malfunction conditions or the degree to which they affect emissions would be impossible to know without extensive field sampling of vehicles presently on the road. We assume, conservatively, that engine malfunctioning will increase aldehyde emissions by a factor of two over the non-malfunction condition for a "typical" case and by a factor of three for the upper bound estimate. Emissions are calculated by

Equation 4.3-1:

$$\text{Annual acetaldehyde emissions} = (EF)(1.609344 \text{ km/mi})(C_m)(C_t)(M)(0.001 \text{ g/mg})(\text{lb}/453.6 \text{ g}) \qquad (4.3\text{-}1)$$

where

EF = Emission factor for each category of vehicle (mg/km)
C_m = Correction factor for mileage
C_t = Correction factor for malfunction or mistune
M = Mileage driven by given category of vehicle (mi)

The results of these computations are shown in Table 4.3-5. Each column corresponds to a factor in Equation 4.3-1. Total annual emissions of acetaldehyde are reported in the right-most column. In the "typical" scenario, annual emissions total 1,900,000 lb (930 tons). The upper bound estimate of acetaldehyde emitted is 4,600,000 lb (2,300 tons).

<u>Emissions Based on Recent Studies</u>. Data for the second set of emission factors rely on only one study for light duty vehicles and one for heavy duty trucks. However, the data are recent, the samples were large, and actual in-use vehicles were tested. Emission factors and emission estimates from these data are reported in Tables 4.3-2 and 4.3-7, respectively.

Emission factors for the light duty vehicle data set are from the study of 46 vehicles by Sigsby et al. (1984) As mentioned previously, three driving tests were performed, the NYCC, the FTP, and the CUE. The NYCC driving procedure does not represent driving conditions in most of California. Therefore, we decided not to use that part of the data in our second statewide emissions estimate for acetaldehyde. The FTP represents urban driving in California, while the CUE represents suburban and high speed rural driving.

For this estimation procedure, we used mileage data compiled by the Motor Vehicle Manufacturers Association (MVMA, 1985). California mileage for 1982 was apportioned to urban and rural sectors by using the national urban-rural data reported in Table 4.3-6.

Table 4.3-5

VEHICLE EMISSIONS OF ACETALDEHYDE IN CALIFORNIA[a] BASED UPON PRE-1981 DATA

Vehicle Category	Emission Factor (EF) (mg/km)	Mileage Correction (C_m)	Malfunction Correction (C_t)	Mileage (M) 10^6	Emissions (lbs)
Typical Case					
Light duty passenger vehicles	0.25	2	2	124,730	442,534
Light duty trucks	0.25	2	2	24,474	86,832
Medium duty trucks	4.22	2	2	7,224	432,639
Heavy duty trucks	19.40	b	b	13,139	904,357
Total					1,866,362
Upper Bound Case					
Light duty passenger vehicles	0.40	3	3	124,730	1,593,123
Light duty trucks	0.40	3	3	24,474	312,596
Medium duty trucks	4.22	3	3	7,224	973,439
Heavy duty trucks	37.40	b	b	13,139	1,743,451
Total					4,622,609

[a] Emission factors calculated by SAIC based upon data in Carey, 1981.

[b] No correction factor.

Table 4.3-6

CALIFORNIA MILES DRIVEN,
AS REPORTED BY THE MOTOR VEHICLE MANUFACTURERS ASSOCIATION[a]

(millions)

Category	Urban	Rural
Passenger Vehicles	97,849	28,709
Trucks	30,361	13,080
Light-duty	16,572	7,140
Medium-duty	4,892	2,107
Heavy-duty	8,897	3,833
Total - All Vehicles	128,210	41,789

[a] Mileage calculated by SAIC based upon ARB data and MVMA, 1985.

Using Equation 4.3-1, with the revised emission factors listed in Tables 4.3-2 and 4.3-3, and the mileage reported in Table 4.3-6, we computed the California emission estimates shown in Table 4.3-7. For these calculations, mileage and engine malfunction correction factors were set to one since the vehicles were in use by the public and were in a variety of mechanical conditions.

Total estimated emissions for light duty vehicles are 2,850,000 lb (1430 tons) acetaldehyde. Our upper bound estimate is 5,050,000 lb (2520 tons).

Emission factors for the 19 heavy duty trucks tested by Warner-Selph and Dietzmann (1984) are reported in Table 4.3-7. Inasmuch as the testing procedure used on these vehicles involved freeway, non-freeway and central city transient driving conditions, we were not able to partition our calculations into urban and rural components. Further, unit correction factors were applied since high-mileage in-use vehicles were tested. Again, using Equation 4.3-1, we obtain the statewide emission estimates shown in Table 4.3-7. For lack of more detailed data, emission factors for light and medium-duty trucks were assumed to be the same as those calculated for light-duty passenger vehicles by Sigsby et al. (1984). Estimated typical and upper bound emissions for trucks are 3,520,000 lb (1,760 tons) and 9,760,000 lb (4,880 tons), respectively. Total estimated annual acetaldehyde emissions from on-road motor vehicles in California are 6,370,000 lb (3,190 tons) or 14,800,000 lb (7,410 tons) as an upper bound.

Comparison of Emission Estimates. Table 4.3-8 compares the emission estimates calculated from the two sets of emission factors presented above. The difference between the two light-duty passenger vehicle typical case estimates is approximately 2,400,000 lb (1,200 tons) and 3,500,000 lb (1,750 tons) in the upper bound estimate. For trucks, the typical case difference is 2,100,000 lb (1050 tons) and the upper bound difference is 5,100,000 lb (2,550 tons).

Table 4.3-7

ACETALDEHYDE EMISSIONS IN CALIFORNIA BASED UPON TWO RECENT STUDIES[a]

Category	Typical Case Emission Factors (mg/km)	Typical Case Typical Emissions (lb)	Upper Bound Case Emission Factors (mg/km)	Upper Bound Case Upper Bound Emissions (lb)
Light-Duty Passenger Vehicles				
Urban	6.696	2,324,597	11.316	3,928,486
Rural	5.159	525,484	11.010	1,121,453
Total		2,850,081		5,049,939
Trucks				
Light-duty[b]				
Urban	6.696	393,700	11.316	665,340
Rural	5.159	130,689	11.010	278,908
Medium-duty[b]				
Urban	6.696	116,219	11.316	196,406
Rural	5.159	38,566	11.010	82,305
Heavy-duty[c]	62.90	2,840,893	189.10	8,540,745
Total		3,520,067		9,763,704
Total All Vehicles		6,370,148		14,813,643

[a] Calculations by SAIC based upon data from MVMA, 1985; Sigsby, et al., 1985; and Warner-Selph and Dietzmann, 1984.

[b] Emission factors for light and medium-duty trucks are the same as those for light-duty passenger vehicles.

[c] Emission data from federal chassis transient cycle for heavy-duty diesels, which combines urban and rural driving conditions.

Table 4.3-8

COMPARISON OF EMISSION ESTIMATES (lb)

Category	Carey Data	Sigsby and Warner-Selph, Dietzmann Data	Difference
Light-Duty Autos			
Typical	442,534	2,850,081	2,407,547
Upper Bound	1,593,123	5,049,939	3,456,816
Trucks[a]			
Typical	1,423,828	3,520,067	2,096,239
Upper Bound	4,622,609	9,763,704	5,141,095
Total			
Typical	1,866,362	6,370,148	4,503,786
Upper Bound	6,215,732	14,813,643	8,597,911

[a] Combines emissions for light, medium, and heavy-duty trucks.

It is interesting to note that although substantially different estimates of emissions resulted from using the data from the two sets of studies, the heavy duty trucks' share of total acetaldehyde emissions is quite large and is similar in the two data sets. In the emissions estimate based on the earlier data, 48.5 percent of the total emissions are from heavy-duty trucks, while this vehicle category's share is 44.6 percent when the most recent data are used.

In all cases the use of data from two recent larger studies results in substantially higher acetaldehyde emissions estimates. Several explanations might account for this phenomenon. Several of the factors comprising our emission equation are highly uncertain, including mileage and engine malfunction correction factors, and apportionment of mileage to the various vehicle categories. In addition, emission factors are uncertain because of the small sample size and variability of the results upon which they are based. The two most likely explanations for these discrepancies are our underestimation of either the mileage or engine malfunction correction factor, or both, for the early data, and the higher emission factors determined by the most recent research. It seems likely that in-use vehicles generate considerably greater acetaldehyde emissions than previously estimated from relatively new in-tune vehicles.

Uncertainties and Problems with Estimation. Discussions with the ARB (Avlani, 1986) and the Motor Vehicle Manufacturers Association (Baker, 1986) indicate the difficulty which occurs from lack of standard vehicle classifications. The ARB classifies vehicles by weight. Light duty automobiles weigh under 4,000 lb, light duty trucks from 4,000-6,000 lb, medium duty trucks from 6,000-8,000 lb, and heavy duty trucks over 8,000 lb. The information compiled by the Federal Highway Administration, reported in the MVMA's Facts and Figures, 1984 booklet (MVMA, 1985), is listed under buses, passenger vehicles, and trucks; no weight information is given for vehicles in the vehicle miles travelled charts. According to the ARB staff, it is common to list light and medium duty trucks under passenger vehicles when the information is not further subdivided. Heavy American automobiles (4,000-6,000 lb) would be listed as light duty trucks in the ARB system (Avlani, 1986). According to the MVMA, on the other hand, vans and pick-up trucks should be listed under the more general category, trucks (Baker, 1986).

We combined the ARB categories of light, medium, and heavy-duty trucks in order to compare them with the MVMA's general trucks classification. This produced mileage figures which were similar in both sets of data. MVMA data were used for emissions computations along with the more recent EPA study of in-use vehicles because of the presence of an urban-rural dichotomy in miles travelled, and because the emissions data were not disaggregated beyond passenger vehicles and trucks.

Reducing estimation uncertainties and errors in vehicle emission testing is an area that needs to be explored in more detail. Possible means of reducing error are:

- Using more representative samples of vehicles for testing;
- Standardizing vehicle classifications;
- More testing to understand the relationship between emissions and normal driving patterns of the public; included here would be the relationships between mileage and emissions, particularly at high mileage, and between typical engine neglect and emissions;
- Agreement on, or standardization of, emission testing protocols; and
- Refinement of vehicle categories for testing, and increased testing in categories other than light duty passenger vehicle.

Aircraft

Rogozen et al. (1984) calculated formaldehyde emissions in California for jet, turboprop, and piston aircraft. Separate emission factors were used for aircraft time spent during the idle, takeoff, climb, and approach phases of flight. Their calculations indicated that jets produce 1,516,000 lb formaldehyde, turboprops produce 64,000 lb, and piston aircraft emit 6,800 lb annually, for a total of 1,586,800 lb. In order to estimate emissions of acetaldehyde, we assumed that 70 percent of total aldehyde emissions are formaldehyde and that acetaldehyde constitutes 20 percent of aldehyde emissions. (See Section 4.3.2.1 for rationale.) Thus,

$$\begin{aligned}\text{Acetaldehyde Emissions} &= (1{,}586{,}800\ \text{lb/yr})(1/0.7)(0.2)\\ &= 450{,}000\ \text{lb/yr}\ (230\ \text{tons/yr})\end{aligned}$$

4.3.2 Fossil Fuel Combustion in Stationary Sources

4.3.2.1 Electric Power Plants

Acetaldehyde emissions from electric power generation in California were estimated using data generated by an earlier SAIC report (Rogozen et al., 1984). SAIC estimated formaldehyde emissions in California from electric power plants in 1981 to be 5,510,000 lb/yr. Of this amount, 785,000 lb was due to emissions from natural gas use and 4,725,000 lb to emissions from fuel oil use. Natural gas use in 1981 totaled 648,995,000 mcf, while fuel oil consumption was 47,027,700 bbl. We updated these earlier data with 1984 natural gas receipts of 546,339,700 mcf and fuel oil receipts of 2,061,800 bbl (Barnett, 1986). Total aldehyde emissions were estimated by assuming that 70 percent of emissions were formaldehyde (Rogozen et al., 1984).

Most data on aldehyde emissions are reported as total aldehydes or formaldehyde. Lacking valid acetaldehyde emission factors for stationary source fuel combustion, we turned to the mobile source literature for an estimate of the acetaldehyde fraction of total aldehydes. It appears that acetaldehyde's percent of total aldehyde emissions varies from 9.9 to 25 percent (Sigsby et al., 1984). In a recent unpublished article, Sigsby et al. (1984) found an average of 25.7 percent acetaldehyde by weight in the emissions of late 1970s and early 1980s cars. We will assume that 20 percent of total aldehyde emissions represents a reasonable approximation to acetaldehyde emissions from stationary sources. The following formula was used to estimate acetaldehyde emissions for 1984:

$$\text{Acetaldehyde emissions} = (0.2/0.7)[(O_{84}/O_{81})FO_{81} + (G_{84}/G_{81})FG_{81}]$$

where,

O_{81}, O_{84} = Fuel oil consumption in California in 1981 and 1984 (bbl)

G_{81}, G_{84} = Natural gas consumption in California in 1981 and 1984 (mcf)

FO_{81} = Formaldehyde emissions from fuel oil combustion in power plants in 1981 (lb)

FG_{81} = Formaldehyde emissions from natural gas combusted in power plants in 1981 (lb)

Thus,

$$\begin{aligned}\text{Acetaldehyde Emissions} &= (0.2/0.7)[(2{,}061{,}800/47{,}027{,}700)(4{,}725{,}000\ \text{lb/yr}) \\ &\quad + (546{,}339{,}700/648{,}995{,}000)(785{,}000\ \text{lb/yr})] \\ &= 248{,}000\ \text{lb/yr} = 124\ \text{tons/yr}\end{aligned}$$

Of this amount, 59,140 lb acetaldehyde are emitted from fuel oil burned by power plants and 188,860 lb are emitted from the combustion of natural gas.

4.3.2.2 Oil Refining

Rogozen et al. (1984) estimated formaldehyde emissions from California refineries in 1981 using a weighted emission factor of 12.6 lb HCHO/1000 bbl oil. This factor assumed that 70 percent of total aldehydes were emitted as formaldehyde. In our estimate of 1984 acetaldehyde emissions we assume that: (1) refinery capacity and operating rates in 1984 were approximately the same as in 1981, (2) formaldehyde represents 70 percent of total aldehydes, and (3) acetaldehyde represents 20 percent of total aldehyde emissions (see Section 4.3.2.1 for rationale). Thus, acetaldehyde emissions in California are calculated as follows:

$$\begin{aligned}\text{Acetaldehyde Emissions} &= (\text{HCHO emissions})(1/0.7)(0.2) \\ &= (8{,}151{,}200\ \text{lb/yr})(1/0.7)(0.2) \\ &= 2{,}328{,}900\ \text{lb/yr} = 1{,}164\ \text{tons/yr}\end{aligned}$$

4.3.2.3 Industrial, Commercial and Residential Fuel Use

Table 4.3-9 shows the quantity of fuel consumed in the industrial, commercial, and residential sectors in California (Wood, 1986), as well as emission factors and annual emissions of acetaldehyde in 1985. Residential fuel consumption data, provided by the California Energy Commission (Wood, 1986), were not separated into space heating and other uses; this division was supplied by Rogozen et al. (1984). The emission factors for natural gas and distillate were also derived from Rogozen et al. (1984), while those for heavy fuel oil come from the EPA's Compilation of Air Pollutant Emission Factors (USEPA, 1976). As for other combustion sources, we assumed that formaldehyde comprised 70 percent, and acetaldehyde 20 percent, of total aldehyde emissions.

Annual emissions from the industrial and commercial sector total 2,520,000 lb (1,260 tons), while residential emissions equal 120,000 lb (60 tons). The combined annual emissions of acetaldehyde from industrial, commercial, and residential combustion is 2,640,000 lb (1,320 tons).

4.3.3 Wood Burning

4.3.3.1 Emission Factors

Lipari et al. (1984) burned several types of wood in a freestanding fireplace with a funnel hood. Air was supplied by natural draft. Total aldehyde emissions varied from about 0.9 to 2.3 grams per kg of dry wood. Emissions were found to vary inversely with burn rate; low burn rates, such as those associated with green quartered logs, yielded about twice the emissions per unit dry weight than did quick burning of split, seasoned wood. The moisture content of the wood apparently had no effect on emission rates. Lipari et al. state that there may be a relationship between wood type and aldehyde emissions per unit dry weight, but data are insufficient to draw conclusions. Acetaldehyde emissions for split wood varied from 0.083 to 0.200 g/kg, or 9.1 to 14.1 percent of total aldehyde emissions.

Table 4.3-9

ACETALDEHYDE EMISSIONS FROM INDUSTRIAL, COMMERCIAL, AND RESIDENTIAL FUEL USE IN 1984

Fuel Type	Quantity	Acetaldehyde Emission Factor[a]	Emissions (1000 lb)
Industrial and Commercial			
Gas	689 x 10^9 ft^3	0.57 lb/10^6 ft^3	393
Heavy Fuel Oil	80 x 10^6 bbl	8.4 lb/10^3 bbl[b]	672
Distillate	58 x 10^6 bbl	25 lb/10^3 bbl	1,450
Residential			
Gas (heat)[c]	287 x 10^9 ft^3	0.07 lb/10^6 ft^3	20
Gas (other)[c]	191 x 10^9 ft^3	0.5 lb/10^6 ft^3	96
Distillate	172 x 10^3 bbl	25 lb/10^3 bbl	4.3
Total			2,635.3

Source: Calculated by SAIC from data in Rogozen et al. (1984).

[a] Assumes that acetaldehyde emissions are 20 percent of total aldehydes.

[b] From SAIC interpretation of AP-42 (USEPA), 1976).

[c] Quantity of gas supplied by California Energy Resources, Conservation and Development Commission (Wood, 1986); proportion used for residential heat or other from Rogozen et al. (1984).

These emissions are considerably lower than the 0.4 to 2.5 g/kg emissions reported by Snowden et al. (1976).

4.3.3.2 Emissions From Residential Wood Consumption

In our calculation of emissions from wood consumption in California, we used an emission factor of 0.2 g acetaldehyde per kg wood consumed. This figure is the highest value reported by Lipari et al. (1984), but is half the lowest value given by Snowden et al. (1976). It thus represents a compromise value between the results reported in the two studies, weighted in favor of the more recent data. We have decided to use this compromise value rather than disregard the older data entirely because improvements in wood burning stove emissions have been more modest than increases in stove efficiencies. This is partly because catalytic stoves are still a rarity.

Two studies have estimated wood consumption in California in 1981. The first, which was conducted by the U.S. Department of Energy, estimated that 2,127,000 cords were consumed in the residential sector. The second, by the U.S. Forest Service, estimated that 1,813,000 cords were consumed (Lew, 1986). The difference between the two figures is due to different estimation methods. We will represent California use by the average value of 1,970,000 cords with a "typical" cord weight of 3000 lb/cord; this represents wood that is neither soft nor very dense. We will assume an annual increase in wood consumption between 1981 and 1985 of 5 percent, for a cumulative increase of 22 percent. Thus,

$$\begin{aligned}\text{Emissions from Residential Wood Consumption} &= (1{,}970{,}000\ \text{cords})(3{,}000\ \text{lb/cord})(0.454\ \text{kg/lb})(0.2\ \text{g/kg})(1.22)\\ &= 6.55 \times 10^{8}\ \text{g/yr}\\ &= 720\ \text{tons/yr}\end{aligned}$$

4.3.3.3 Emissions From Industrial and Commercial Wood Combustion

The Biomass Office of the California Energy Resources, Conservation and Development Commission (CEC), using a biomass tracking list, which includes the size of the industrial or commercial facility, and an energy conversion factor, estimated the amount of wood consumed by the industrial and commercial sector in California for 1985 to be 4.9 million dry tons (Lew, 1986). The following calculation estimates the amount of acetaldehyde produced by combustion at industrial and commercial establishments during 1985.

Emissions From Industrial and Commercial Sector $= (4.9 \times 10^6 \text{ tons/yr})(2{,}000 \text{ lb/ton})(0.454 \text{ kg/lb})(0.2 \text{ g/kg})$

$= 8.9 \times 10^8 \text{ g/yr}$

$= 980 \text{ tons/yr}$

4.3.4 Coffee Roasting

Although a 1978 study conducted for the U.S. Environmental Protection Agency (Eimutis et al., 1978) concluded that coffee roasting was the second largest source of acetaldehyde emissions nationwide, supporting data are lacking. The cited study presented neither the emission factors nor the process rates upon which the estimates were based. To explore this potential emission source further, SAIC conducted an online search of the CAS and COFFEELINE data bases, as well as a manual review of the literature.

As was noted in another EPA-sponsored review (Lesh and Mead, 1985), the literature contains no specific information on the processes by which acetaldehyde emissions are produced. However, the presence of "aldehydes" in condensed off-gases from coffee roasting was reported by Sullivan et al. (1965). Average and peak total uncontrolled aldehyde emissions (measured as formaldehyde) from a coffee roaster were 7.5 and 13.2 ppm, respectively. The aldehydes constituted about 9 percent of total organics in the exhaust.

At SAIC's request, the ARB Emission Inventory Branch searched the Emission Data System for facilities having source classification codes 3-02-002-01 (coffee roasting - direct fired) and 3-02-002-02 (coffee roasting-indirect fired). Table 4.3-10 shows the facilities identified and, where data were available, their total organic gas (TOG) emissions. To estimate acetaldehyde emissions, we assumed, as in Section 4.3.3, that acetaldehyde comprised 20 percent of total aldehyde emissions. Thus acetaldehyde emissions

Table 4.3-10
ACETALDEHYDE EMISSIONS FROM COFFEE ROASTING

Facility	City	County	Emissions (lb/yr) TOG	Acetaldehyde
Caffe Trieste	San Francisco	San Francisco	172.7	3.1
Farmer Brothers	Torrance	Los Angeles	0.0	0.0
First Colony	San Francisco	San Francisco	385.0	6.9
Folger Coffee Company	S. San Francisco	San Mateo	ND[a]	ND
F. Gavina and Sons	Los Angeles	Los Angeles	0.0	0.0
Graffeo Coffee	San Francisco	San Francisco	10.5	0.2
Hills Brothers	San Francisco	San Francisco	700.8	12.6
Intl. Coffee and Tea	Camarillo	Ventura	249.1	4.5
J. B. Loucks	San Francisco	San Francisco	80.3	1.4
M J B Company	Union City	Alameda	ND	ND
Maxwell House	San Leandro	Alameda	ND	ND
Peter James Coffee	Mountain View	Santa Clara	62.7	1.1
Rich Coffee, Inc.	Brisbane	San Mateo	9.9	0.2
Uncommon Grounds	Berkeley	Alameda	11.7	0.2
Totals			1,682.7	30.3

---

[a] ND = No data. Emissions from these sources may be significantly higher than those for the other facilities reported here.

would be (0.09)(0.2)(TOG) = 0.018 TOG. As seen in Table 4.3-10, acetaldehyde emissions from sources for which throughput data were available are only about 30 lb/yr. Inclusion of emissions from facilities for which data are incomplete could increase this estimate by an order of magnitude, but coffee roasting emissions would still be minor when compared with other sources evaluated in this chapter.

4.3.5 Tobacco Smoke

It has generally been acknowledged that tobacco smoke is a significant contributor to indoor air pollution; however its contribution to outdoor pollution is not usually recognized. Acetaldehyde is known to be present in cigarette smoke. According to the National Research Council (1981), emission factors vary from 0.18 mg to 1.44 mg acetaldehyde per cigarette. We will use an emission factor of 0.5 mg acetaldehyde per cigarette as a first approximation, recognizing the potential error such a calculation might produce. According to the Tobacco Institute (Moran, 1986), Americans smoked 594 billion cigarettes in 1985. This consumption may be apportioned to California on the basis of population. The following computation estimates emissions of acetaldehyde from tobacco smoke in California, assuming a California/U.S. population ratio of 0.11:

$$\begin{aligned}\text{Acetaldehyde Emissions} &= (594 \times 10^{9}\ \text{cig./yr})(0.5\ \text{mg/cig.})\\ &\quad (2.2 \times 10^{-6}\ \text{lb/mg})(\text{ton}/2000\text{lb})\\ &\quad (0.11)\\ &= 36\ \text{tons/yr}\end{aligned}$$

4.4 INDUSTRIAL USE AND EMISSIONS

Acetaldehyde is used in the production of acetic acid, peracetic acid, pentaerythritol, pyridenes, terephthalic acid, 1,3-butylene glycol, and crotonaldehyde (Lesh and Mead, 1985). No pentaerythritol is produced in California (Bloomhardt and Pelland, 1985) and, to the best of our knowledge, no other acetaldehyde derivative is either. Nevertheless, the Bay Area Air Quality Management District estimates industrial emissions of about 0.1 ton per year in its jurisdiction (Hill, 1986).

4.5 CONSUMER USE AND EMISSIONS

Small amounts of acetaldehyde may be present as a contaminant in acetone (Lesh and Mead, 1985), which is widely used in nail polish remover and other consumer products. However, no data on contamination levels are available at this writing.

4.6 EMISSION SUMMARY

Table 4.6-1 summarizes our estimates of acetaldehyde emissions from various sources in California. Total emissions are about 7,800 to 12,000 tons per year (7,100 to 11,000 MT/yr), almost all of which are from combustion sources. These estimates are fairly uncertain, given lack of data on emission factors for both mobile and stationary sources.

4.7 SUMMARY OF AMBIENT CONCENTRATION DATA

Acetaldehyde is ubiquitous in urban air and its ambient concentrations have been measured in a number of studies carried out in Southern California and elsewhere.

4.7.1 Gas Phase Concentrations

Gas phase concentrations of acetaldehyde are summarized in Table 4.7-1. Data for other urban locations are also included for comparison. Up to 39 ppb of acetaldehyde have been recorded in Los Angeles air during severe smog episodes. Figure 4.7-1 gives a typical frequency distribution of the ambient acetaldehyde concentrations measured on smog episode days. As is shown in Figure 4.7-2, gas phase levels of acetaldehyde (CH_3CHO) exhibit strong diurnal variations with maxima associated with photochemical activity and, to a lesser extent, with automobile traffic. The relative importance of direct emissions, photochemical production, and removal reactions is discussed in detail in Section 4.8.

Table 4.6-1

SUMMARY OF ANNUAL ACETALDEHYDE EMISSION ESTIMATES FOR CALIFORNIA

Source	Tons/Year	MT/Year
Direct Production	0	0
Indirect Production		
Light-Duty Automobiles[a]	1,400 - 2,500	1,300 - 2,300
Trucks[a]	1,800 - 4,800	1,600 - 4,400
Aircraft	230	210
Electric Power Plants	120	110
Oil Refining	1,200	1,100
Industrial and Residential Fossil Fuel Use	1,300	1,200
Residential Wood Combustion	720	650
Industrial Wood Combustion	980	890
Coffee Roasting	<0.1[b]	<0.1
Tobacco Smoke	36	33
Industrial Use	0.1	0.1
Consumer Products	Negligible[c]	Negligible
Total	7,800 - 12,000	7,100 - 11,000

[a] Estimate based on most recent data (see text). Values shown are typical and upper bound.

[b] Estimate based on available data only. Actual value may be an order of magnitude higher.

[c] Some acetaldehyde may be present as a contaminant in acetone.

Table 4.7-1

GAS PHASE CONCENTRATIONS OF ACETALDEHYDE IN URBAN AIR

Location	Period	Concentration ppb	Reference
East Los Angeles, CA (Cal State University Campus)	May-June 1980	up to 26	a
Claremont, CA	Sept.-Oct. 1980	3-35	a
Azusa, CA	Oct. 1980	up to 10	b
Lennox, CA	Oct. 1980	up to 3	b
Downtown Los Angeles, CA	July-Oct. 1980	13-37	b
Burbank, CA	July-August 1980	8-16	b
Pasadena, CA	July 1980	13	b
El Monte, CA	Oct. 1980	25-33	b
Rosemead, CA	Oct. 1980	16	b
Upland, CA	Oct. 1980	19	b
Los Angeles, CA (USC Campus)	Sept.-Nov. 1981	2-39	c
Tucson, AZ	Feb.-Sept. 1982	23 ± 12	d
Schenectady, NY	June-August 1983	up to 5	e
Upton, NY	July 1982-May 1983	0.5-35 (average = 3)	f
Nagoya, Japan	Dec. 1976	up to 10	g
Osaka, Japan	May-July 1978 February 1983	up to 8 2-9	h i
Delft and Rotterdam, The Netherlands	Jan.-Dec. 1980	annual mean = 2	j

[a] Grosjean, 1982.

[b] Grosjean et al., 1983.

[c] Grosjean and Fung, 1984.

[d] Snider and Dawson, 1985.

[e] Schulam et al., 1985.

[f] Tanner and Meng, 1984.

[g] Hoshika, 1977.

[h] Kuwata el al., 1979.

[i] Kuwata el al., 1983.

[j] Guicherit and Schulting, 1985.

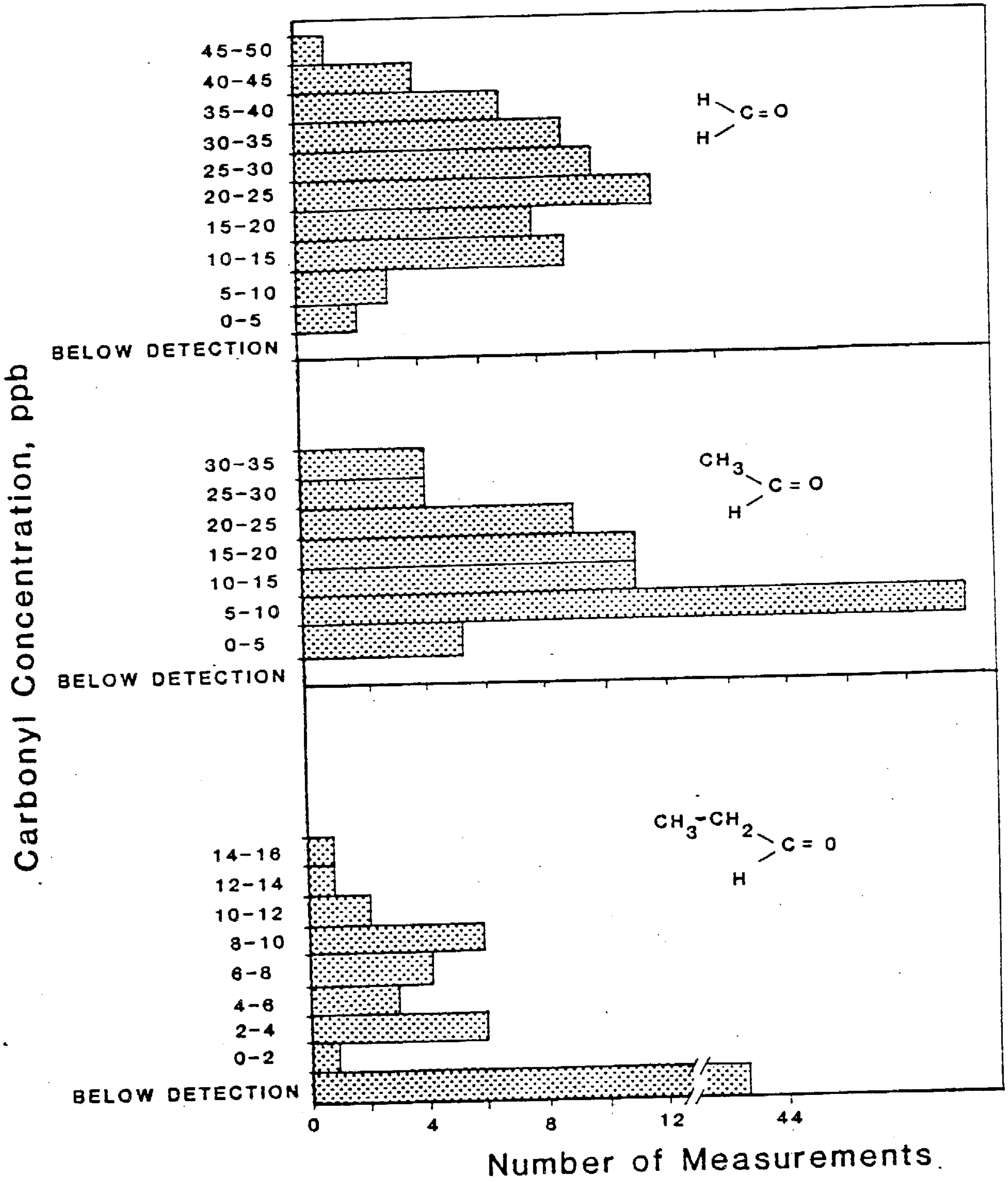


Figure 4.7-1. Frequency Distribution of Formaldehyde, Acetaldehyde and Propanal Concentrations Measured During Smog Episodes at Claremont, CA, September-October 1980 (Grosjean, 1982).

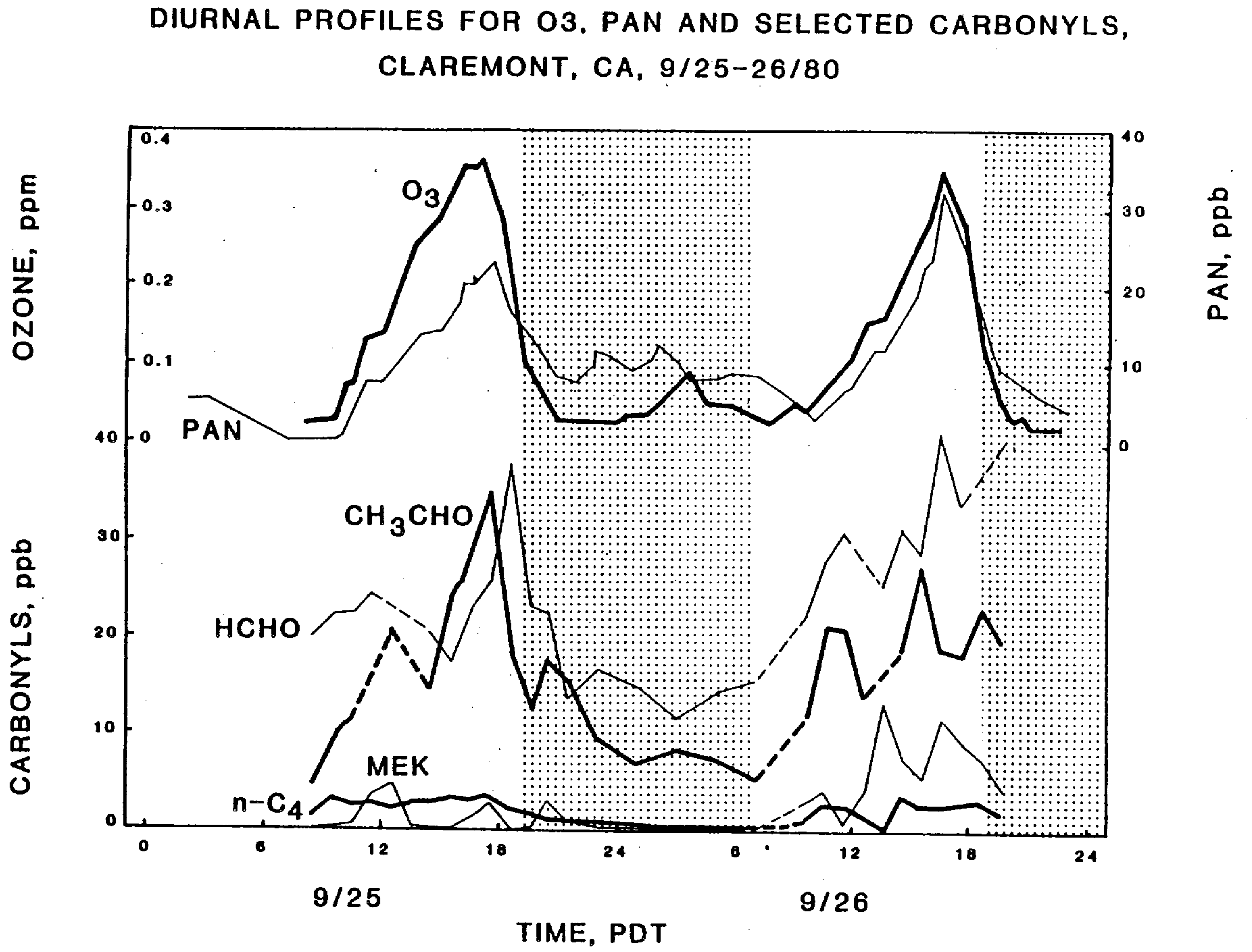


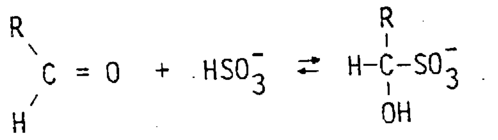
Figure 4.7-2. Diurnal Profiles for Ozone, PAN and Selected Carbonyls at Claremont, CA, 25-26 September 1980 (Grosjean, 1982).

4.7.2 Particulate Phase Concentrations

The only report available concerning particulate phase concentrations of acetaldehyde appears to be that of Grosjean (1982), who collected 4-hour samples on Teflon filters in Claremont, CA during September - October 1980 smog episode days. Acetaldehyde concentrations were in the range 2-400 ng/m^3 (average 94 ng/m^3, 14 samples). The results were discussed in terms of filter artifact (deemed negligible on Teflon filters), scavenging of gas phase acetaldehyde by aerosol droplets, and possible retention of acetaldehyde in the droplets as bisulfite or other adducts. Simultaneous measurements of gas phase and particulate phase acetaldehyde showed that essentially all (99.5 to >99.9 percent) of the airborne acetaldehyde was in the gas phase.

4.7.3 Hydrometeor Concentrations

Results concerning acetaldehyde concentrations in Southern California cloud, fog and rainwater have recently become available (Table 4.7-2). Grosjean and Wright (1983) have noted that carbonyls in hydrometeors may exist as free carbonyls and/or as bisulfite adducts (hydroxyalkane sulfonic acids):



$$RHC=O + HSO_3^- \rightleftarrows H-\overset{R}{\underset{OH}{C}}-SO_3^-$$

Additional studies are therefore needed to clarify whether the concentrations reported in Table 4.7-2 represent free or total (free + bisulfite adduct) acetaldehyde. To our knowledge, such studies have not yet been carried out.

4.7.4 Consistency Checks

Gas phase concentrations of acetaldehyde can be verified for consistency in two ways, one involving comparison with formaldehyde and other aldehydes (for which emission, atmospheric kinetics, and urban concentration data exist) and the other involving comparison with peroxyacetyl nitrate (PAN), since acetaldehyde is a major precursor of PAN via the following reaction sequence (see details in Section 4.8):

Table 4.7-2

ACETALDEHYDE CONCENTRATIONS IN HYDROMETEORS

Hydrometeor Type	Location	Acetaldehyde Concentrate µg/ml	Reference
Rainwater	Camarillo, CA	1×10^{-3}	a
	Carson, CA	0.11	a
	Santa Rita, AZ (rural site)	0.066	b
	Osaka, Japan	0.011-0.052	c
Cloudwater	Henninger Flats, CA (slope-intercepted stratus clouds, elevation ∿600m)	0-0.59 (mean 0.10, 16 samples	a
	Several locations over Los Angeles area (aircraft)	0.2-2.2	d
Mist	Long Beach, CA	0.11	a
	Marina del Rey, CA	0.10	a
Fogwater	Pasadena, CA	0.08-0.17	a
	Marina del Rey, CA	0.15	a
	Morro Bay, CA	0.006	a
	San Nicholas Island, CA	0.06, 0.09	a
Ice Fog	Fairbanks, AK	0.007-0.13	a

[a] Grosjean and Wright, 1983.

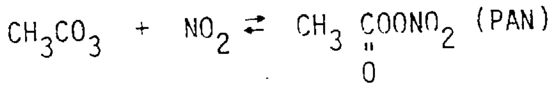
[b] Snider and Dawson, 1985.

[c] Takami et al., 1985.

[d] Richards et al., 1985.

$$CH_3CHO + OH \rightarrow H_2O + CH_3CO$$

$$CH_3CO + O_2 \rightarrow CH_3CO_3$$



$$CH_3CO_3 + NO_2 \rightleftarrows CH_3\underset{\overset{\|}{O}}{C}OONO_2 \text{ (PAN)}$$

Fortunately, most studies involving measurements of acetaldehyde in urban air have also included data on formaldehyde, PAN, or both, along with data on other pollutants and meteorological variables (e.g., Figures 4.7-1 and 4.7-2). Examination of these data sets show no major inconsistency (and in fact, good agreement) between reported acetaldehyde concentrations and those expected from emission, kinetic and photochemistry considerations.

4.8 ATMOSPHERIC CHEMISTRY

4.8.1 In-Situ Formation

4.8.1.1 Gas Phase Processes

In situ formation is a major component of the overall atmospheric persistence of acetaldehyde in polluted air. This is because many hydrocarbons, including olefins, paraffins and aromatics, yield acetaldehyde as one of several atmospheric oxidation products. Olefins are removed from polluted air by reactions with ozone and with the hydroxyl radical. For paraffins and aromatics, reaction with ozone is too slow to be significant under atmospheric conditions, and the only important removal process is that initiated by their reaction with OH. The corresponding reaction mechanisms, applicable to acetaldehyde and to a number of other toxic organics reviewed in this report, are summarized below.

The Ozone-Olefin Reaction

This reaction proceeds by addition of ozone to the unsaturated carbon-carbon bond followed by unimolecular decomposition of the biradical to form a carbonyl and a second biradical. This sequence is illustrated in Figure 4.8-1 for a simple olefin, propene ($CH_3CH = CH_2$). Further reactions of the second biradical (or Criegee biradical) include rearrangement into carboxylic acid, further fragmentation (e.g., $H_2\dot{C}O\dot{O} \rightarrow CO + H_2O$, $CO_2 + 2H$, etc.), or reactions with other pollutants such as NO and SO_2 to yield a second carbonyl molecule, e.g.,

$$CH_3\dot{C}HO\dot{O} + NO \rightarrow NO_2 + CH_3CHO$$

It is evident, from the simplified mechanism shown in Figure 4.8-1, that acetaldehyde is a major product not only of the ozone-propene reaction, but also of the reaction of ozone with any olefin bearing a methyl substituent ($CH_3CH = CR_1R_2$, R_1 and R_2 = alkyl groups) such as cis and trans 2-butene, 2-pentene, 2-methyl-2-butene, etc.

The OH-Olefin Reaction

This reaction also proceeds by addition of the hydroxyl radical on the unsaturated carbon-carbon bond, followed by reaction of the alkyl radical thus formed with oxygen to yield a peroxy radical (Figure 4.8-2). Reaction of the peroxy radical with NO yields the corresponding alkoxy radical ($RO_2 + NO$ $RO + NO_2$) followed by unimolecular decomposition of the alkoxy radical into a carbonyl and an α-hydroxy alkyl radical. This radical, in turn, reacts with oxygen to yield HO_2 and a second carbonyl. The net reaction can be summarized as follows:

$$\text{olefin} + OH \xrightarrow[NO_2]{O_2,\ \underset{\downarrow}{NO},\ O_2} HO_2 + 2\ \text{carbonyls.}$$

Acetaldehyde is expected to form as a major product of the reaction of OH with all olefins bearing methyl substituents such as propene, 2-butene, and 2-pentene.

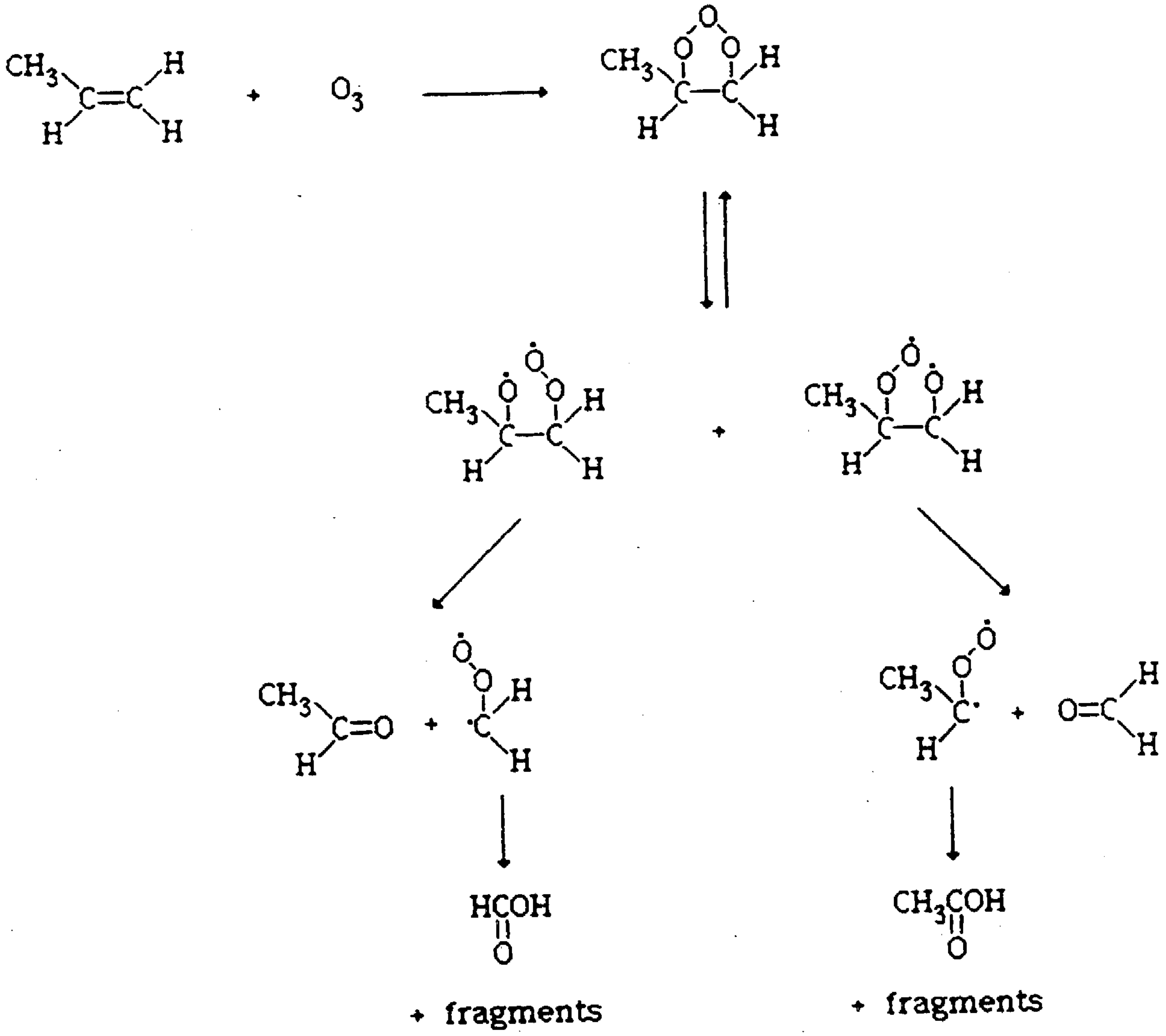


Figure 4.8-1. Ozone-Olefin Reaction Mechanism (Olefin = Propene).

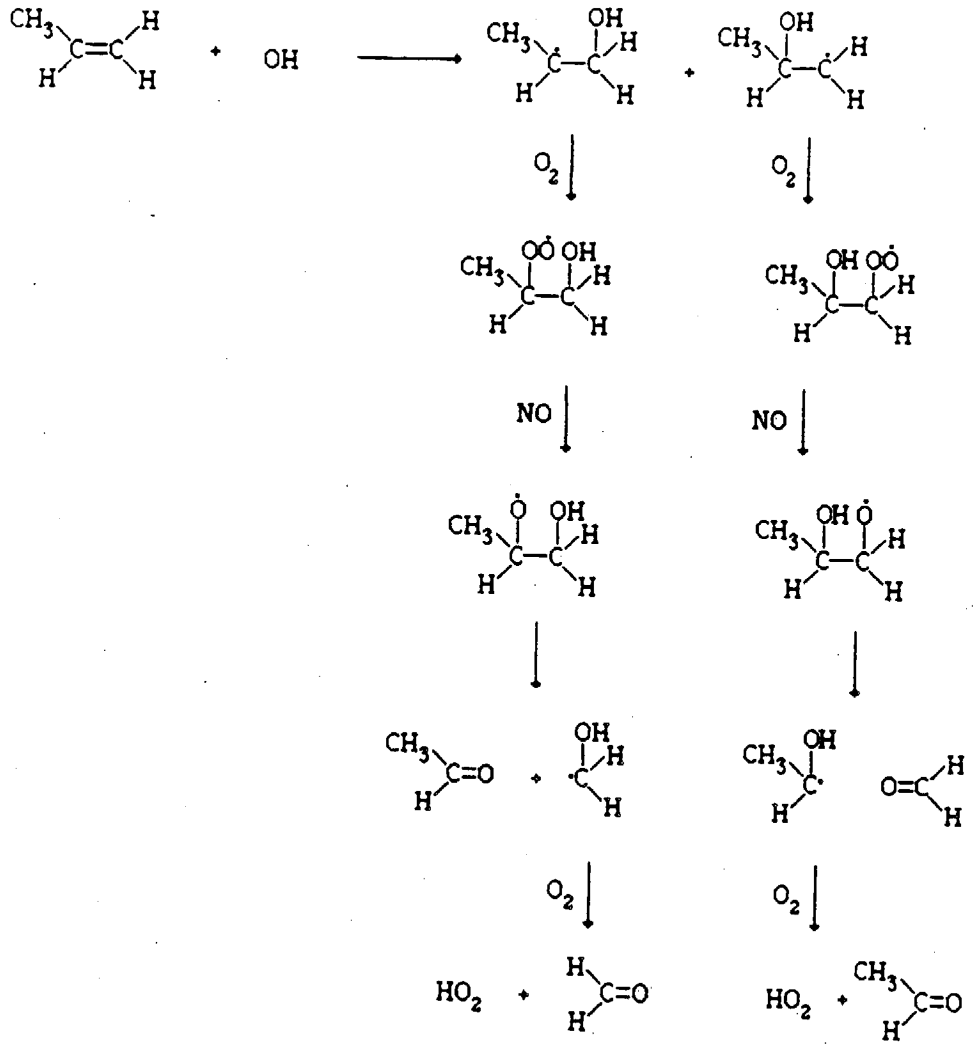


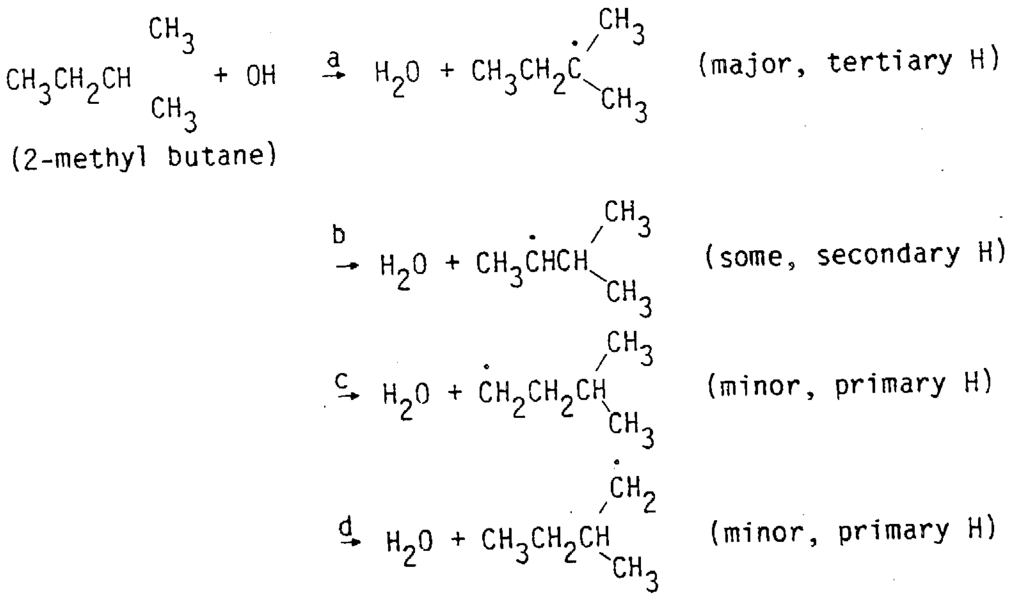
Figure 4.8-2. OH-Olefin Reaction Mechanism (Olefin = Propene).

The OH-Paraffin Reaction

This reaction proceeds by abstraction of a hydrogen atom:

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

followed by the alkyl → peroxy → alkoxy sequence discussed in the preceding paragraph. Unimolecular decomposition of the alkoxy radical yields a carbonyl and a second alkyl radical, which will undergo the same reaction sequence and yield a second carbonyl product. The OH-paraffin reaction mechanism is illustrated in Figure 4.8-3 for a simple paraffin, propane ($CH_3CH_2CH_3$), which reacts with OH to yield acetaldehyde and formaldehyde. For more complex molecules, OH will abstract preferentially (but not exclusively) the weakest hydrogen atom (tertiary H), thus leading to several carbonyl products:



$$CH_3CH_2CH\begin{matrix}CH_3\\ \\ CH_3\end{matrix} + OH \xrightarrow{a} H_2O + CH_3CH_2\dot{C}\begin{matrix}\diagup CH_3\\ \diagdown CH_3\end{matrix} \quad \text{(major, tertiary H)}$$

(2-methyl butane)

$$\xrightarrow{b} H_2O + CH_3\dot{C}HCH\begin{matrix}\diagup CH_3\\ \diagdown CH_3\end{matrix} \quad \text{(some, secondary H)}$$

$$\xrightarrow{c} H_2O + \dot{C}H_2CH_2CH\begin{matrix}\diagup CH_3\\ \diagdown CH_3\end{matrix} \quad \text{(minor, primary H)}$$

$$\xrightarrow{d} H_2O + CH_3CH_2CH\begin{matrix}\diagup \dot{C}H_2\\ \diagdown CH_3\end{matrix} \quad \text{(minor, primary H)}$$

The OH-Aromatic Hydrocarbon Reaction

This reaction, whose features are still not entirely understood, involves both OH addition and abstraction pathways and is discussed in detail in those chapters covering aromatic compounds (xylenes, phenols, etc.) Acetaldehyde is formed in the OH-aromatic reaction, but as a secondary product of reactions involving dicarbonyls (e.g., methylglyoxal, $CH_3\underset{\underset{O}{\|}}{C}CHO$) which are themselves formed following opening of the aromatic ring. For example, acetaldehyde is a product of the photolysis of methylglyoxal:

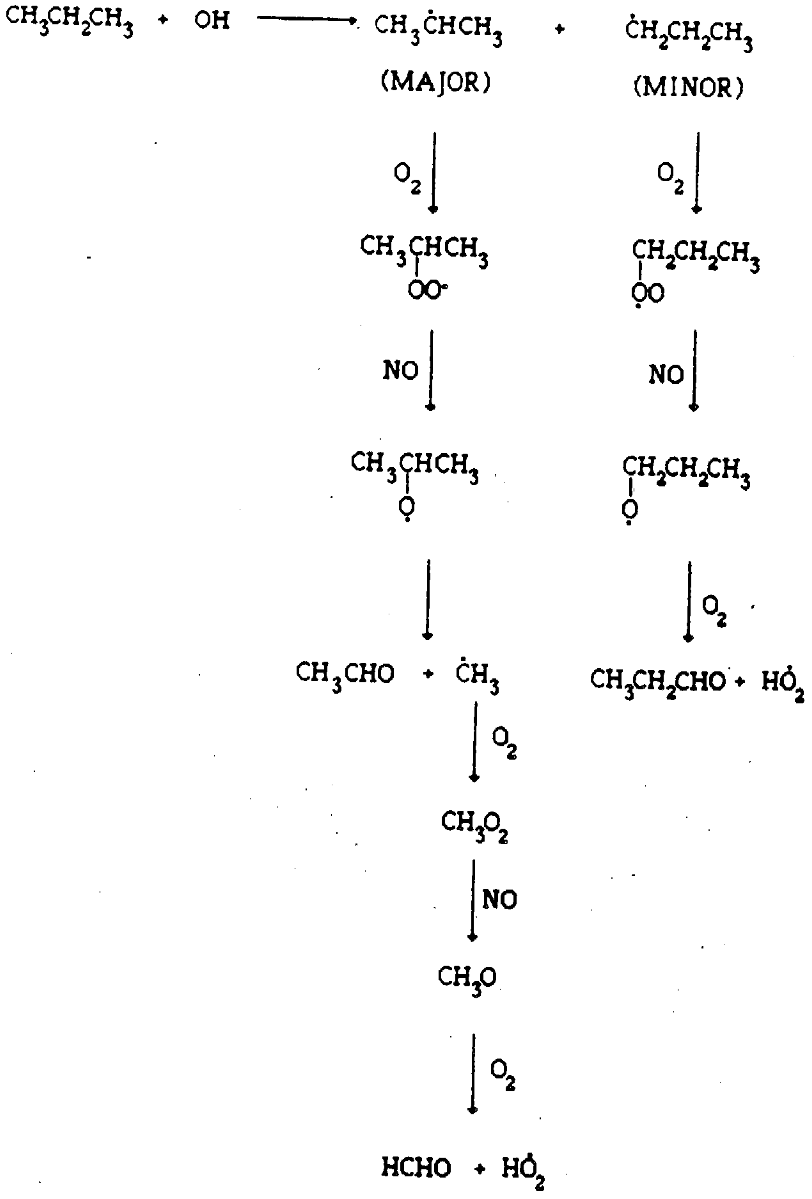
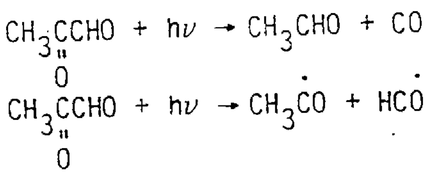


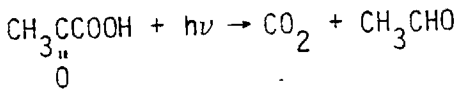
Figure 4.8-3. OH-Paraffin Reaction Mechanism (Paraffin = Propane).



$$CH_3\underset{\overset{\|}{O}}{C}CHO + h\nu \rightarrow CH_3CHO + CO$$

$$CH_3\underset{\overset{\|}{O}}{C}CHO + h\nu \rightarrow CH_3\dot{C}O + HC\dot{O}$$

and of the photolysis of the ketoacid pyruvic acid:



$$CH_3\underset{\overset{\|}{O}}{C}COOH + h\nu \rightarrow CO_2 + CH_3CHO$$

where methylglyoxal is a product of the toluene - OH reaction and pyruvic acid is a product of the ortho-cresol-OH reaction. Thus, nearly all alkylbenzenes, phenols (cresols) and their derivatives may contribute to the in-situ production of acetaldehyde in polluted air.

Acetaldehyde Precursors

We have summarized in the preceding paragraphs the mechanisms of the ozone-olefin, OH-olefin, OH-paraffin, and OH-aromatic reactions, all of which may contribute to acetaldehyde production in polluted air. Olefinic, paraffinic and aromatic hydrocarbons are indeed present in urban air, and have been the object of several reports with emphasis on the Los Angeles area. Grosjean and Fung (1984) have reviewed the earlier literature and have measured individual concentrations of about 50 hydrocarbons at a downtown Los Angeles location. Their results, summarized in Table 4.8-1, were obtained between 6 and 9 a.m. on 23 days during September 29 - November 13, 1981, and comprise the most recent data set for the Los Angeles area. While shifts in fuel composition and usage may have occurred since 1981, the data in Table 4.8-1 are probably fairly representative of the hydrocarbon mix, including many precursors of acetaldehyde, present in Los Angeles air today.

4.8.1.2 Liquid Phase Processes

Some of the hydrocarbon oxidation pathways reviewed above may also take place in the liquid phase, including aquated aerosols, cloud, fog and rain (see for example the computer kinetic modeling studies of Graedel and Weschler, 1981, and Chameides and Davis, 1982). Snider and Dawson (1985) have observed that acetaldehyde and formaldehyde concentrations in rain collected

Table 4.8-1

HYDROCARBONS AND CARBONYLS IN DOWNTOWN LOS ANGELES AIR

Compound	Range of concentrations, ppbv
Alkynes	
acetylene	26-94
Alkanes	
ethane	32-221
propane	11-99
isobutane	10-33
n-butane	21-70
isopentane	23-83
n-pentane	9-34
2,3-dimethylbutane	2-8
2-methylpentane	8-28
3-methylpentane	4-15
n-hexane	5-20
2,2,3-trimethylbutane	0-9
2,4-dimethylpentane	2-6
2,3-dimethylpentane	2-9
3-methylhexane	3-24
2,2,4-trimethylpentane	3-15
n-heptane	3-11
2,5-dimethylhexane	1-3
2,3,4-trimethylpentane	2-5
3-methylheptane	2-5
2,2,5-trimethylhexane	1-4
n-octane	1-5
n-nonane	1-3
n-decane	1-9
Cycloalkanes	
methylcyclopentane	4-16
cyclohexane	7-31
dimethylcyclopentane	1-19
methylcyclohexane	3-14
dimethylcyclohexane	0-1
Alkenes	
ethylene	32-91
propene	7-32
1-pentene	1-8
2-methyl-1-pentene	0-4
Aromatics	
benzene	12-29
toluene	20-68
ethylbenzene	3-12
m- and p-xylene	11-45
o-xylene	4-13
n-propylbenzene	1-3
p-ethyltoluene	4-12
o-ethyltoluene	3-1
1,3,5-trimethylbenzene	4-12
1,2,4-trimethylbenzene	4-12
1,2,3-trimethylbenzene	1-4
n-butylbenzene	0-2
Carbonyls	
formaldehyde	4-86
acetaldehyde	2-39
propanal + acetone + acrolein	1-54
n-butanal	0-5
benzaldehyde	0-2

Source: Grosjean and Fung, 1984

near Tucson, AZ, were higher, relative to C_1-C_2 alcohols and acetonitrile, than those of the corresponding gas phase samples. They suggested that these observations were consistent with in-cloud production of acetaldehyde (and formaldehyde) by some unspecified mechanism. Liquid phase oxidation processes that include acetaldehyde production have yet to be documented in California air.

4.8.2 Removal Processes

4.8.2.1 Gas Phase Processes

Reaction of acetaldehyde with ozone is too slow to be important under atmospheric conditions. Photolysis and reaction with OH are the dominant daytime removal processes. Both pathways are outlined in Figure 4.8-4. The corresponding reaction products include free radicals, formaldehyde (a Level 1 toxic air contaminant) and peroxyacetyl nitrate (PAN), a potent eye irritant and mutagenic and phytotoxic compound.

Nighttime removal of acetaldehyde by reaction with the nitrate radical is expected to be of some importance on the basis of kinetic data and laboratory experiments, but remains to be firmly established in urban air. Both nitric acid and PAN would be formed at night by reaction of NO_3 with acetaldehyde. There is only one set of nighttime data including acetaldehyde, nitric acid, PAN, and other relevant pollutants, such as CO, ozone, and particulate nitrate in urban air (Grosjean 1982, 1983;). (See Figure 4.7-2.) The nighttime production of nitric acid (and/or nitrate) reported by Grosjean has been interpreted by Stockwell and Calvert (1983) in terms of aldehyde-NO_3 reaction, but other nitrate production mechanisms (e.g., hydrolysis of N_2O_5) cannot be ruled out. There was no strong evidence for production of PAN. The nighttime acetaldehyde/CO ratios were fairly constant, which suggest either no removal of aldehydes by reaction with NO_3 or a balance between aldehyde removal (by NO_3) and aldehyde production (by olefin-ozone reactions). Other removal processes (dry deposition, scavenging by fog and/or aerosol droplets) may also be involved. Additional field studies are obviously needed to establish the importance of nighttime removal processes for acetaldehyde in urban air.

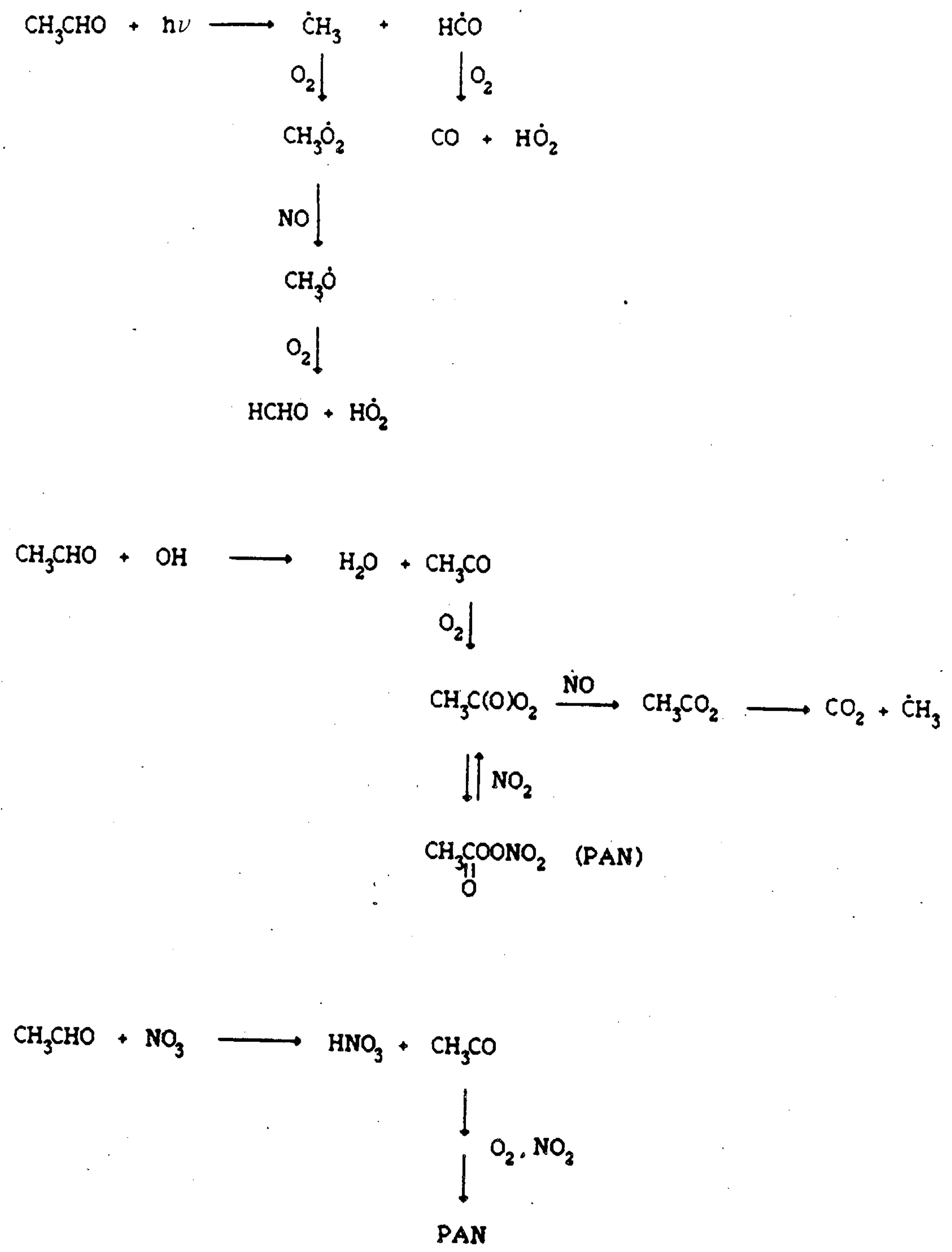


Figure 4.8-4. Atmospheric Removal Processes for Acetaldehyde: Photolysis (Top), Reaction with OH (Middle) and Reaction with NO_3 (Bottom).

4.8.2.2 Liquid-Phase Processes

As noted in Section 4.7.3, acetaldehyde has been identified in California fog, rain and cloudwater samples. Scavenging by hydrometeors is therefore probably important for gas-phase acetaldehyde. Once incorporated into droplets, acetaldehyde may be further removed by oxidation to form acetic acid, or by reaction with free radicals. Acetaldehyde also forms a stable adduct with bisulfite in aqueous solutions (hydroxyethane sulfonic acid). Thus, depending upon SO_2 levels, droplet acidity, concentrations of oxidants, etc., adduct formation is expected to compete with droplet phase removal processes. In the absence of any data, the possible importance of liquid-phase processes for removal of acetaldehyde cannot be assessed at this time.

4.8.3 Contribution of Emissions, In-Situ Formation and Atmospheric Removal Reactions to Ambient Levels of Acetaldehyde

Grosjean et al. (1983) have investigated the relative importance of emissions and photochemistry (both production and removal) to ambient levels of carbonyls, including acetaldehyde, in the Los Angeles area. Emission estimates were derived from the California Resources Board inventory and from ambient measurements of carbonyls and of carbon monoxide on days of negligible photochemical activity. Photochemical production and removal were estimated from measurements of ambient carbonyls (again using carbonyl/CO ratios) during smog episodes, and from computer kinetic modeling of specific smog episode days. For these, measured individual hydrocarbon and carbonyl data (such as those listed in Table 4.8-1) were used as input to the model. The authors concluded that in-situ production of acetaldehyde in Los Angeles air may reach 50-200 tons/day during smog episodes, and that this large term is typically offset by a substantial in-situ removal term of 40-150 tons/day. Direct emissions of acetaldehyde, about 15-18 tons/day, were thus a minor component of the overall acetaldehyde "budget" in Los Angeles air.

4.9 REFERENCES

Avlani, P. 1986. Personal communication from Associate Air Pollution Specialist, Technical Support Division, California Air Resources Board, Sacramento, CA (6 February).

Baines, T., J. Somers and K. Hellman. 1982. "EPA motor vehicle emissions characterization projects on light and heavy duty diesels," Journal of the Air Pollution Control Association 32(7):725-728.

Baker, Mrs. 1986. Personal communication from Motor Vehicle Manufacturers Association of the U.S., Detroit, MI (15 February).

Barnett, R. 1986. Personal communication from Information Specialist, National Energy Information Center, U.S. Department of Energy, Washington, D.C. (4 June).

Black, F, W. Ray, F. King, W. Karches, R. Bradow, N. Perry, J. Duncan and W. Crews. 1984. Emissions from in-use heavy duty gasoline trucks. U.S. Environmental Protection Agency, Environmental Sciences Research Laboratory, EPA-600/D-84-281 (NTIS: PB85-127470).

Bloomhardt, M.A. and A. S. Pelland. 1985. Source-specific air toxics data for states in EPA Region 9. Prepared by Radian Corporation for U.S. Environmental Protection Agency, Region IX, DCN no. 85-203-024-49-06.

Carey, P. 1981. Mobile source emissions of formaldehyde and other aldehydes. U.S. Environmental Protection Agency, Emission Control Technology Division, Ann Arbor, MI, EPA/AA/CTAB/PA/81-11.

Chameides, W.L. and D.D. Davis. 1982. "The free radical chemistry of cloud droplets and its impact upon the composition of rain," Journal of Geophysical Research 87:4863-4877.

Doerr, Mr. 1985. Personal communication from Texas Eastman, Longview, TX (10 July).

Eimutis, E.C., R.P. Quill, and G.M. Rinaldi. 1978. Source assessment: Noncriteria pollutant emissions (1978 update). Prepared by Monsanto Research Corporation for U.S. Environmental Protection Agency, Industrial Environmental Research Laboratory, Research Triangle Park, NC, EPA-600/2-78-004t.

Gabele, P., J. Braddock, F. Stump and R. Zweidinger. 1977. Characterization of exhaust emissions from a dual catalyst equipped vehicle. U.S. Environmental Protection Agency, Environmental Sciences Research Laboratory, Research Triangle Park, NC, EPA-600/2-77-068 (NTIS: PB 266941).

Graedel, T.E. and C.J. Weschler. 1981. "Chemistry within aqueous atmospheric aerosols and raindrops," Rev. Geophys. Space Phys. 19:505-539.

Grosjean, D. 1982. "Formaldehyde and other carbonyls in Los Angeles ambient air," Environmental Science and Technology 16:254-262.

Grosjean, D. 1983. "Distribution of atmospheric nitrogenous pollutants at a Los Angeles area smog receptor site," *Environmental Science and Technology* 17:13-19.

Grosjean, D., R.D. Swanson and C. Ellis. 1983. "Carbonyls in Los Angeles air: contribution of direct emissions and photochemistry," *Science of the Total Environment* 28:65-85.

Grosjean, D. and K. Fung. 1984. "Hydrocarbons and carbonyls in Los Angeles air," *Journal of the Air Pollution Control Association* 34:537-543.

Grosjean, D. and B. Wright. 1983. "Carbonyls in urban fog, ice fog, cloudwater and rainwater," *Atmospheric Environment* 17:2093-2096.

Guicherit, R. and F.L. Schulting. 1985. "The occurrence of organic chemicals in the atmosphere of the Netherlands," *Science of the Total Environment* 32:193-219.

Hill, S. 1985. *1984 toxic use survey: Bay Area Air Quality Management District*. Bay Area Air Quality Management District, San Francisco, CA.

Hoshika, Y. 1977. "Simple and rapid gas-liquid-solid chromatographic analysis of trace concentrations of acetaldehyde in urban air," *Journal of Chromatography* 137:455-460.

Johann, B. 1985. Personal communication from Supervisor of Customer Services, Publicker Chemical Corporation, Greenwich, CT (10 July).

Kuwata, K., M. Uerobi and Y. Yamasaki. 1979. "Determination of aliphatic and aromatic aldehydes in polluted air as their 2,4-DNPhydrazones by high performance liquid chromatography," *J. Chromatog. Sci.* 17:264-268.

Kuwata, K., M. Uerobi and Y. Yamasaki. 1983. "Determination of aliphatic aldehydes in air by liquid chromatography," *Analytical Chemistry* 55:2013-2016.

Lesh, S.A. and R.C. Mead. 1985. *Source screening for acetaldehyde*. Prepared by Radian Corporation for U. S. Environmental Protection Agency, Research Triangle Park, NC, Contract No. 68-02-3889.

Lew, V. 1986. Personal communication from Energy Specialist, Biomass Office, Energy Resources, Conservation and Development Commission, Sacramento, CA (9 June).

Lipari, F., J.M. Dasch and W.F. Scruggs. 1984. "Aldehyde emissions from wood-burning fireplaces," *Environmental Science and Technology* 18(5):326-330.

Moran, B. 1986. Personal communication from Assistant President, Tobacco Institute, Washington, D.C. (29 May).

MVMA (Motor Vehicle Manufacturers Association of the U.S.). 1984. "Motor vehicle facts and figures, 1984," Detroit, MI.

National Research Council. 1981. *Formaldehyde and other aldehydes*. Committee on Aldehydes, Board on Toxicology and Environmental Health Hazards, Assembly of Life Sciences. National Academy Press, Washington, D.C.

Nebel, G. 1981. "The effect of misfueling on aldehyde and other auto exhaust emissions," Journal of the Air Pollution Control Association 31(8):877-879.

Richards, L.W., J.A. Anderson, D.L. Blumenthal and J.A McDonald. 1985. Characterization of the composition and three-dimensional distribution of acidity in southern California clouds. Prepared by Sonoma Technology, Inc. for the California Air Resources Board, Report STI 90083-506-13DES, Contract No. A2-125-32.

Rogozen, M., G. Maldonado, D. Grosjean, A. Shochet, and R. Rapoport. 1984. Formaldehyde: a survey of airborne concentrations and sources. Prepared by Science Applications International Corporation for California Air Resources Board, Sacramento, CA, SAI-84/1642.

SAI (Systems Applications, Inc.). 1980. Human exposure to atmospheric concentration of selected chemicals: Volume 2. Prepared for the U.S. Environmental Protection Agency, Research Triangle Park, NC (NTIS: PB81-193252).

Schulam, P., R. Newbold and L.A. Hull. 1985. "Urban and rural ambient air aldehyde levels in Schenectady, New York and in Whiteface Mountain, New York," Atmospheric Environment 19:623-626.

Sigsby, J., S. Tejada and W. Ray. 1984. Volatile organic compound emissions from 46 in-use passenger cars. U.S. Environmental Protection Agency, Environmental Sciences Research Laboratory, Research Triangle Park, NC.

Sittig, M. 1981. Handbook of toxic and hazardous chemicals. Noyes Publications, Park Ridge, NJ.

Smith, L. 1983. Characterization of exhaust emissions from operation of a light duty gasoline vehicle on alternate source gasoline fuels. Prepared by Southwest Research Institute for the U.S. Environmental Protection Agency, EPA-460/3-83-008 (NTIS: PB84-104538).

Smith, L. and C. Urban. 1982. Characterization of exhaust emissions from methanol and gasoline fueled automobiles. Prepared by Southwest Research Institute for the U.S. Environmental Protection Agency, Office of Mobile Source Air Pollution Control, Ann Arbor, MI, EPA 460/3-82-004 (NTIS PB83-116830).

Snider, J.R. and G.A. Dawson. 1985. "Tropospheric light alcohols, carbonyls and acetonitrile: concentrations in the southwestern United States and Henry's law data," Journal of Geophysical Research 90:3797-3805.

Snowden, W.D., D.A. Alguard, G.A. Swenson and W.E. Stolberg. 1976. Source-sampling residential fireplaces for emission factor development. U.S. Environmental Protection Agency, Research Triangle Park, NC, EPA-450/3-76-010.

Stafford, J.K. 1985. Personal communication from Coordinator, Industrial Hygiene/Environmental Affairs, Shell Chemical Company, Dallas, TX (10-16 July).

Stehr, C.E. 1985. Personal communication from Celanese Chemical Company, Houston, TX (10 July).

Sullivan, J.L., F.L. Kafka, and I.M. Ferrari. 1965. "An evaluation of catalytic and direct fired afterburners for coffee and chicory roasting odors," Journal of the Air Pollution Control Association 15(12):583-586.

Takami, K., K. Kuwata, A. Sugimae and M. Nakamoto. 1985. "Trace determination of aldehydes in water by high performance liquid chromatography," Analytical Chemistry 57:243-245.

Tanner, R.L. and Z. Meng. 1984. "Seasonal variations in ambient atmospheric levels of formaldehyde and acetaldehyde," Environmental Science and Technology 18:723-726.

Urban, C. 1981. Unregulated exhaust emissions from non-catalyst gasoline cars under malfunction conditions. Prepared by Southwest Research Institute for the U.S. Environmental Protection Agency, Office of Mobile Source Air Pollution Control, Ann Arbor, MI, EPA 460/3-81-020 (NTIS: PB82-101130).

USEPA (U.S. Environmental Protection Agency). 1976. Compilation of Air Pollutant Emission Factors, Second Edition, Part A. Office of Air and Waste Management, Office of Air Quality Planning and Standards, Research Triangle Park, NC, AP-42.

Verschueren, K. 1977. Handbook of environmental data on organic chemicals. Van Nostrand Reinhold Company, New York, NY.

Warner-Selph, M.A. and H.E. Dietzmann. 1984. Characterization of heavy-duty vehicle emissions under transient conditions. Prepared by Southwest Research Institute for U.S. Environmental Protection Agency, Research Triangle Park, NC (NTIS: PB85-124154).

Wood, W. 1986. Personal communication from Fuels Program Specialist, Fossil Fuels Division, California Energy Resources, Conservation and Development Commission, Sacramento, CA (9 June).

5.0
EVALUATION OF ACROLEIN

5.1 PHYSICAL AND CHEMICAL PROPERTIES

Acrolein is a flammable colorless to yellowish liquid. Table 5.1-1 summarizes some of its physical and chemical properties.

5.2 DIRECT PRODUCTION IN CALIFORNIA

Acrolein is produced as an isolated product in the manufacture of glycerine and as a non-isolated intermediate in the manufacture of acrylic acid and its derivatives. To the best of our knowledge, acrolein is not produced in California (Bloomhardt and Pelland, 1985).

5.3 INDIRECT PRODUCTION AND EMISSIONS IN CALIFORNIA

Acrolein is emitted to the atmosphere through a variety of combustion sources, including motor vehicles, fossil-fueled power plants, industrial and domestic furnaces, wood-burning stoves, fireplaces, coffee roasting, and tobacco smoke.

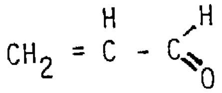
5.3.1 Mobile Sources

5.3.1.1 Automobiles and Trucks

As mentioned in Section 4.3.1, most of the early studies on mobile sources of aldehydes concentrated on formaldehyde (Carey, 1981). Analytic techniques in these early studies were unable to separate acrolein from acetone and propionaldehyde. Thus, few early studies of mobile sources report emissions for acrolein, and those that do, do not provide meaningful data for emission estimation.

A recent study by the EPA, presently in draft form (Sigsby et al., 1984), reported separate acrolein emission factors for 46 light-duty vehicles. Model years ranged from 1975 to 1982, with the greatest representation among

Table 5.1-1
CHEMICAL DATA SUMMARY FOR ACROLEIN

Property	Value for Acrolein
CAS Registry No.	107-02-8
Synonyms	2-propenal, acrylic aldehyde, allyl aldehyde, acrylaldehyde, acraldehyde
Molecular Weight	56.06
Molecular Formula	C_3H_4O
Molecular Structure	 $CH_2 = \overset{H}{C} - C\overset{\diagup H}{\underset{\diagdown\!\!\diagdown O}{}}$
Physical State at STP	Colorless to yellowish liquid, flammable
Boiling Point	52.5°C
Melting Point	-86.95°C
Specific Gravity	0.8410 at 20°C/4°C
Vapor Pressure	288.2 mm at 25°C
Vapor Density (air=1)	1.94
Solubility	Very soluble, (400 g/L of H_2O)
Log Partition Coefficient (octanol/H_2O)	
Henry's Law Constant	

Source: SAI (1980), Verschueren (1977).

the more recent ones. All automobiles were equipped with some form of catalytic converter. Three test procedures were used with these vehicles: the Federal Test Procedure driving cycle (FTP), the New York City driving cycle (NYCC), and the Crowded Urban Expressway driving cycle (CUE). Each test simulates a different type of driving environment and, therefore, a combination of two or three is likely to represent actual emissions better than the FTP alone.

The FTP protocol, which has traditionally been the only procedure used, employs the Urban Dynamometer Driving Schedule for its testing protocol. This schedule, in turn, has a transient phase with hot and cold starts, and a cold start stabilized phase, simulating a typical urban driving pattern as would have been seen in Los Angeles in the late 1960s. The NYCC is a low-speed driving cycle, similar to crowded central city driving conditions. The CUE represents normal high speed driving.

For the 46 vehicles in the Sigsby et al. study, Table 5.3-1 reports mean emission factors for total aldehydes; mean percent of total aldehydes by weight of acrolein; mean acrolein standard deviations; emission factors for acrolein; and an upper bound estimate of emission factors for acrolein (estimated to be two standard deviations above the mean). Emission factors range from 0.723 mg/km in the CUE procedure to 2.636 mg/km in the NYCC test.

Light Duty Vehicles

Although the NYCC test may simulate driving patterns in some portions of central Los Angeles and San Francisco, it does not represent driving conditions in California. Therefore, we decided not to use the NYCC data in our statewide emissions estimate for acrolein. We estimated statewide emissions by dividing statewide mileage into rural and urban components, which we assumed to be represented by the FTP procedure and CUE test, respectively. The mean values for the acrolein emission factors, for the 46 tested vehicles (Table 5.3-1), were used to estimate light-duty vehicle emissions, while the upper-bound values were used to estimate a worst case scenario for acrolein emissions in the state.

Table 5.3-1

EMISSION FACTORS FOR ACROLEIN[a]

Compounds	NYCC	FTP	CUE
Total Aldehydes (mg/km)	70.81	26.58	18.49
Acrolein's Percent by Weight of Aldehydes (Pct of total)	3.723	5.112	3.908
Standard Deviation (mg/km)	3.134	1.173	0.789
Mean Acrolein (mg/km)	2.636	1.359	0.723
Upper Bound Acrolein ($X + 2\sigma$) (mg/km)	8.904	3.704	2.301

Chassis Transient Test for Diesels	
Heavy-Duty Trucks	
Mean Acrolein (mg/km)	7.6
Standard Deviation (mg/km)	11.6
Upper Bound ($X + 2\sigma$)	30.8

[a] Calculated by SAIC with data from Sigsby et al., c. 1985 and Warner-Selph and Dietzmann, 1984.

Table 5.3-2

URBAN AND RURAL VEHICLE MILES IN CALIFORNIA[a] (millions)

Vehicle	Mileage	
	Urban	Rural
Passenger Vehicles	97,849	28,709
Trucks	30,361	13,080
Total	128,210	41,789

[a] Calculated by SAIC with data from MVMA, 1984.

Urban and rural vehicle miles driven in California are reported in Table 5.3-2. Miles driven were sub-divided into urban passenger vehicle miles, rural passenger vehicle miles, urban truck miles, and rural truck miles, using data supplied by the Motor Vehicle Manufacturers Association of the U.S. (MVMA, 1984). Correction factors for mileage and for engine malfunctioning, which were applied in the case of acetaldehyde (Section 4.3.1), were not used in this case because the vehicles tested for acrolein emissions were in-use loaners from the public. Therefore, tested vehicles comprised a reasonably representative mix from model years 1975 through 1982, and would be in the same mechanical condition as on-road vehicles. Light duty passenger vehicle emissions were calculated for urban and rural mileage by using the FTP and CUE emission factors, respectively.

Typical emissions were estimated as follows:

<u>Light duty urban passenger vehicle emissions:</u>

$(1.359 \text{ mg/km})(97{,}848.7 \times 10^6 \text{ mi})(1.61 \text{ km/mi})$
$(0.001 \text{ mg/g})/(453.6 \text{ g/lb})$

= 472,000 lb (236 tons)

<u>Light duty rural passenger vehicle emissions:</u>

$(0.723 \text{ mg/km})(28{,}709 \times 10^6 \text{ mi})(1.61 \text{ km/mi})$
$(0.001 \text{ mg/g})/(453.6 \text{ g/lb})$

= 74,000 lb (37 tons)

<u>Total light duty passenger vehicle emissions:</u>

= 546,000 lbs (273 tons)

An upper bound for light-duty vehicle emissions was estimated as follows:

Light duty urban passenger vehicle emissions:

$(3.704 \text{ mg/km})(97{,}848.7 \times 10^6 \text{ mi})(1.61 \text{ km/mi})$
$(0.001 \text{ mg/g})/(453.6 \text{ g/lb})$

= 1,290,000 lb (645 tons)

Light duty rural passenger vehicle emissions:

(2.302 mg/km)(28,709 x 10^6 mi)(1.61 km/mi)
(0.001 mg/g)/(453.6 g/lb)

= 235,000 lb (117 tons)

Total light duty passenger vehicles:

= 1,525,000 lb (763 tons)

Heavy Duty Vehicles

Warner-Selph and Dietzmann (1984) recently reported acrolein emission factors for single-axle and double-axle heavy duty tractor-trailor trucks. We used data for only 15 of the 19 trucks used in their study, because of a high minimum detection level in one testing procedure. All vehicles had accumulated between 33,000 and 266,000 miles. They were tested using the 1984 Federal Testing Procedure, the Recommended Practice for Determining Exhaust Emissions for Heavy-Duty Diesel Engines. As Table 5.3-1 indicates, the mean acrolein emission factor for the 15 trucks with reportable data was 7.6 mg/km and the upper bound estimate of emissions was 30.8 mg/km. Using the vehicle mileage data (urban plus rural) reported in Table 5.3.2, we estimated statewide emissions as follows:

Truck emissions:

(7.6 mg/km)(43,441 x 10^6 mi)(1.61 km/mi)
(0.001 mg/g)/(453.6 g/lb)

= 1,170,000 lb (585 tons)

Upper bound of truck emissions:

(30.8 mg/km)(43,441 x 10^6 mi)(1.61 km/mi)
(0.001 mg/g)/(453.6 g/lb)

= 4,750,000 lb (2,370 tons)

Table 5.3-3 summarizes our estimates of total annual acrolein emissions from automobiles and trucks. It should be noted that these estimates are only a first approximation. One major area of uncertainty pertains to emissions from light- and medium-duty trucks. We found no acrolein emission factors for these classifications, primarily because prior

Table 5.3-3

ESTIMATED ANNUAL ACROLEIN EMISSIONS FROM ON-ROAD MOTOR VEHICLES

Vehicle Category	Typical Case (lb)	Upper-Bound (lb)
Light Duty		
Urban	472,000	1,290,000
Rural	74,000	235,000
Total	546,000	1,525,000
Trucks	1,170,000	4,750,000
Total	1,716,000	6,275,000

studies, which tested these truck categories, were not concerned with acrolein. In a second calculation, we used emissions from heavy-duty vehicles as a surrogate for light- and medium-duty trucks.

If we assume an average emission factor of 3 mg/km for light- and medium-duty trucks, a figure which is intermediate between that for passenger vehicles and heavy duty trucks, and total California mileage equal to 30,698 x 10^6 miles for the light and medium duty category (Avlani, 1986), we obtain 327,000 lb/yr acrolein emitted by light- and medium-duty trucks. Calculating total acrolein emissions, and assuming the remaining truck miles (from Table 5.3-2) are driven by heavy duty vehicles, we find annual emissions of 670,000 lb by trucks of all sizes. Adding this to the emissions from passenger vehicles yields 1,216,000 lb/yr (609 tons/yr), or approximately 500,000 lb/yr (250 tons/yr) less than previously calculated by merging all trucks into one category. Further research on acrolein emission factors for light and medium duty trucks is needed to eliminate this uncertainty.

5.3.1.2 Aircraft

Rogozen et al. (1984) calculated formaldehyde emissions in California for jet, turboprop, and piston aircraft. Separate emission factors were used for aircraft time spent during the idle, takeoff, climb, and approach phases of flight. Their calculations indicated that jets produce 1,516,000 lb formaldehyde, turboprops produce 64,000 lb, and piston aircraft emit 6,800 lb annually, for a total of 1,586,800 lb. In order to estimate emissions of acrolein, we assume that 70 percent of total aldehyde emissions are formaldehyde and that acrolein constitutes 4.4 percent of aldehyde emissions.

Thus,

$$\text{Aircraft Acrolein Emissions} = (1{,}586{,}800 \text{ lb/yr})(1/0.7)(0.044)$$

$$= 99{,}700 \text{ lb/yr (50 tons/yr)}$$

5.3.2 Fossil Fuel Combustion in Stationary Sources

5.3.2.1 Electric Power Plants

In Section 4.3.2.1, SAIC estimated acetaldehyde emissions in California from power plants by updating formaldehyde emissions from a 1984 SAIC report (Rogozen et al., 1984). We used the same approach to estimate emissions of acrolein.

We will estimate California acrolein emissions by combining these earlier fuel consumption data with updated 1984 natural gas receipts of 1546,339.7 x 10^3 mcf and fuel oil receipts of 2,061.8 x 10^3 bbl (Barnett, 1986). Most studies of aldehyde emissions report total aldehydes or formaldehyde, rather than acrolein. Lacking valid emission factors for conversion of fuel combusted at stationary sources into acrolein emissions, we turned to the mobile source literature for an estimate of the acrolein fraction of total aldehydes.

In a recent study (Sigsby et al., 1984), acrolein accounted for approximately 4.4 percent of total aldehydes emitted from a variety of recent model automobiles. We will use the 4.4 percent as a reasonable estimate of the percent emissions from stationary combustion sources, recognizing that uncertainty in the percent emitted could lead to errors as high as 100 percent of the actual emissions.

Based upon these assumptions (see Section 4.3.2.1 for computational details), we calculate that 13,000 lb acrolein are emitted from fuel oil burned by power plants and 41,400 lb are emitted from the combustion of natural gas, for total emissions of 54,400 lb/yr (27.2 tons/yr).

5.3.2.2 Oil Refining

Rogozen et al. (1984) estimated formaldehyde emissions from California refineries in 1981 using a weighted emission factor of 12.6 lb HCHO/1000 bbl oil. This factor assumed that 70 percent of total aldehydes were emitted as formaldehyde. In our estimate of 1984 acrolein emissions we assume that: (1) refinery capacity and operating rates in 1984 were approximately the same as in 1981, (2) formaldehyde represents 70 percent of total aldehydes, and (3) acrolein represents 4.4 percent of total aldehyde emissions (see Section 5.3.2.1 for rationale). Thus, acrolein emissions in California are calculated as follows:

$$\text{Acrolein} = (\text{HCHO emissions})(1/0.7)(0.044)$$

$$\begin{aligned}\text{Emissions} &= (8{,}151{,}200\ \text{lb})(1/0.7)(0.044)\\ &= 512{,}000\ \text{lb}\ (256\ \text{tons})\end{aligned}$$

5.3.2.3 Industrial, Commercial and Residential Fuel Use

Table 4.3-9 showed the quantity of fuel consumed in the industrial, commercial, and residential sectors in California (Wood, 1986), as well as emission factors and annual emissions of acrolein in 1985. Residential fuel consumption, data for which were supplied by the California Energy Resources, Conservation and Development Commission (Wood, 1986), was not separated into heat and other uses; rather, this division was supplied by Rogozen et al. (1984). Emission factors for natural gas and distillate were also derived from Rogozen et al. (1984), while those for heavy fuel oil came from the EPA's Compilation of Air Pollutant Emission Factors (USEPA, 1976). We assumed that formaldehyde comprised 70 percent, and acrolein 4.4 percent, of total aldehyde emissions.

Annual emissions from the industrial and commercial sector total 553,000 lb (277 tons), while residential emissions equal 26,500 lb (13 tons). The combined annual emissions of acrolein from industrial, commercial, and residential combustion is 579,500 lb (290 tons).

5.3.3 Wood Burning

5.3.3.1 Emission Factors

Lipari et al. (1984) burned several types of wood in a freestanding fireplace with a funnel hood. Air was supplied by natural draft. Aldehydes were quantified by formation of derivatives of 2,4-dinitrophenylhydrazones (DNPH), followed by high performance liquid chromatography. Total aldehyde emissions varied from about 0.9 to 2.3 grams per kg of dry wood. Emissions were found to vary inversely with burn rate; low burn rates, such as those associated with green quartered logs, yielded about twice the emissions per unit dry weight than did quick burning of split, seasoned wood. The moisture content of the wood apparently had no effect on emission rates. Lipari et al. state that there may be a relationship between wood type and aldehyde emissions per unit dry weight, but data are insufficient to draw conclusions. Acrolein emissions for split wood varied from 0.021 to 0.048 g/kg, or 2.0 to 5.1 percent of total aldehyde emissions.

5.3.3.2 Emissions From Residential Wood Consumption

In our calculation of emissions from wood consumption in California, we used the value 0.035 g acrolein per kg wood consumed. This figure is the mean of the lowest and highest value reported by Lipari et al. (1984).

Two studies have estimated wood consumption in California in 1981. The first, conducted by the U.S. Department of Energy, estimated that 2,127,000 cords of wood were consumed in the residential sector. The second, by the U.S. Forest Service, estimated that 1,813,000 cords were consumed (Lew, 1986). The difference between the two figures is due to different estimation methods. We represented California use by the average value of 1,970,000 cords, with a "typical" cord weight of 3000 lb/cord. We also assumed an annual increase in wood consumption between 1981 and 1985 of 5 percent, or 22 percent for the 4 years.

Thus,

Emissions from Residential Wood Consumption = (1,970,000 cords)(3,000 lb/cord)(0.454 kg/lb)(0.035 g/kg)(1.22)

= 252,000 lb (126 tons)

5.3.3.3 Emissions From Industrial and Commercial Wood Combustion

The Biomass Office of the California Energy Resources, Conservation and Development Commission, using a biomass tracking list, which includes the size of the industrial or commercial facility, and an energy conversion factor, estimated the amount of wood consumed by the industrial and commercial sector in California for 1985 to be 4.9 million dry tons (Lew, 1986). The following calculation estimates the amount of acrolein produced by combustion at industrial and commercial establishments during 1985.

Emissions From Industrial and Commercial Sector = (4,900,000 tons)(2,000 lb/ton)(0.454 kg/lb)(0.035 g/kg)

= 1.56×10^8 g (156 MT)

= 343,000 lb (172 tons)

5.3.4 Coffee Roasting

Although a 1978 study conducted for the U.S. Environmental Protection Agency (Eimutis et al., 1978) concluded that coffee roasting was the second largest source of acrolein emissions nationwide, supporting data are lacking. The cited study presented neither the emission factors nor the process rates upon which the estimates were based. To explore this potential emission source further, SAIC conducted an online search of the CAS and COFFEELINE data bases, as well as a manual review of the literature.

As was noted in another EPA-sponsored review (Lesh and Mead, 1985), the literature contains no specific information on the processes by which acrolein emissions are produced. However, the presence of "aldehydes" in condensed off-gases from coffee roasting was reported by Sullivan et al. (1965). Average and peak total uncontrolled aldehyde emissions (measured as formaldehyde) from a coffee roaster were 7.5 and 13.2 ppm, respectively. The aldehydes constituted about 9 percent of total organics in the exhaust.

At SAIC's request, the ARB Emission Inventory Branch searched the Emission Data System for facilities having source classification codes

3-02-002-01 (coffee roasting - direct fired) and 3-02-002-02 (indirect fired). Table 5.3-10 shows the facilities identified and, where data were available, their total organic gas (TOG) emissions. To estimate acrolein emissions, we assumed, as in Section 4.3.3, that acrolein comprised 4.4 percent of total aldehyde emissions. Thus acrolein emissions would be (0.09)(0.2)(TOG) = 0.018 TOG. As seen in Table 5.3-4, acrolein emissions from sources for which throughput data were available are only about 7 lb/yr. Inclusion of emissions from facilities for which data are incomplete could increase this estimate by an order of magnitude, but coffee roasting emissions would still be minor when compared with other sources evaluated in this chapter.

5.3.5 Tobacco Smoke

Acrolein is a significant component of cigarette smoke. According to the National Research Council (1981), the emission factor is 0.7 mg acrolein per cigarette, although it appears that this figure is based upon few measurements. If we assume this figure to be correct, we may calculate the total acrolein emissions in California by using a national cigarette consumption value of 594 billion per year (Moran, 1986) and apportioning acrolein emissions to California on the basis of population, assuming a California/U.S. population ratio of 0.11.

$$\begin{aligned}\text{Acrolein Emissions} &= (594 \times 10^{9}\ \text{cig.})(0.7\ \text{g/mg})(10^{-6}\ \text{kg/mg})\\ &\quad (2.205\ \text{lb/kg})(0.11)\\ &= 101{,}000\ \text{lb} = 50.4\ \text{tons}\end{aligned}$$

Uncertainty in this estimate stems from the emission factor estimate and from the assumption that California's share of national cigarette consumption equals its share of U.S. population. Per-capita cigarette consumption in California, however, may not be the same as the national average. Given these uncertainties, the California estimate of emissions of acrolein is probably accurate to within a factor of two or three.

Table 5.3-4

ACROLEIN EMISSIONS FROM COFFEE ROASTING

Facility	City	County	Emissions (lb/yr) TOG	Acrolein
Caffe Trieste	San Francisco	San Francisco	172.7	0.7
Farmer Brothers	Torrance	Los Angeles	0.0	0.0
First Colony	San Francisco	San Francisco	385.0	1.5
Folger Coffee Company	S. San Francisco	San Mateo	ND[a]	ND
F. Gavina and Sons	Los Angeles	Los Angeles	0.0	0.0
Graffeo Coffee	San Francisco	San Francisco	10.5	<0.1
Hills Brothers	San Francisco	San Francisco	700.8	2.8
Intl. Coffee and Tea	Camarillo	Ventura	249.1	1.0
J. B. Loucks	San Francisco	San Francisco	80.3	0.3
M J B Company	Union City	Alameda	ND	ND
Maxwell House	San Leandro	Alameda	ND	ND
Peter James Coffee	Mountain View	Santa Clara	62.7	0.2
Rich Coffee, Inc.	Brisbane	San Mateo	9.9	<0.1
Uncommon Grounds	Berkeley	Alameda	11.7	<0.1
Totals			1,682.7	6.7

[a] ND = No data. Emissions from these sources may be significantly higher than those for the other facilities reported here.

5.4 INDUSTRIAL USE AND EMISSIONS

Acrolein is used as an intermediate in the production of methionine, and small quantities are used for the production of miscellaneous chemicals, including certain types of polyurethane, pharmaceuticals, herbicides and tear gas (Lesh and Mead, 1985). According to data compiled by Lesh and Mead (1985), no methionine is produced in California. Furthermore, calls by SAIC to the three manufacturers of acrolein, all of whom are located in the Gulf states, we have determined that the compound is most likely not shipped into California for use as a chemical intermediate (Gorham, 1985; Hamilton, 1985; Neumann, 1985; Stafford, 1985). We conclude that industrial uses and emissions of acrolein in California are negligible.

5.5 CONSUMER USE AND EMISSIONS

According to the Toxicology Data Base, acrolein is not used in consumer products. Therefore, there are no ambient emissions of acrolein from such products.

5.6 EMISSION SUMMARY

Table 5.6-1 summarizes our estimates of acrolein emissions from various sources in California. Total emissions are about 1,800 to 4,100 tons per year (1,700 to 3,700 MT/yr), almost all of which are from combustion sources. These estimates are fairly uncertain, given lack of data on emission factors for both mobile and stationary sources.

5.7 SUMMARY OF AMBIENT CONCENTRATION DATA

5.7.1 Gas Phase Concentrations

Ambient concentrations of acrolein were measured in the 1960s at several locations in the Los Angeles area (Renzetti and Bryan, 1961; Altschuller and McPherson, 1963; Scott Research Laboratories, 1969). These studies have been reviewed by Altschuller (1983). Typical concentrations, which are presented in Table 5.7-1, range from 2 to 11 ppb. Diurnal

Table 5.6-1

SUMMARY OF ANNUAL ACROLEIN EMISSION ESTIMATES FOR CALIFORNIA

Source	Tons/Year	MT/year
Direct Production	0	0
Indirect Production		
Light-Duty Automobiles[a]	270 - 760	245 - 690
Trucks[a]	585 - 2,370	530 - 2,150
Aircraft	50	45
Electric Power Plants	27	24
Oil Refining	260	240
Industrial and Residential Fossil Fuel Use	290	260
Residential Wood Combustion	130	120
Industrial Wood combustion	170	150
Coffee Roasting	<0.1[b]	<0.1
Tobacco Smoke	50	45
Industrial Use	Negligible	Negligible
Consumer Products	Negligible	Negligible
Total	1,800 - 4,100	1,700 - 3,700

[a] Estimate based on most recent data (see text). Values shown are typical and upper bound.

[b] Estimate based on available data only. Actual value may be an order of magnitude higher.

Table 5.7-1

AMBIENT CONCENTRATIONS OF ACROLEIN

(Concentrations in ppb)

Sampling Location	Year	Acrolein Concentration Average	Maximum	Reference
Los Angeles (downtown)	1961	5	11	Altschuller, 1983
	1963	7	14	Altschuller, 1983
South Pasadena, CA	1963	6	11	Altschuller, 1983
Huntington Park, CA	1961	6	11	Altschuller, 1983
El Monte, CA	1968	4	8	Altschuller, 1983
Edison, NJ	1977	2	4	Pellizzari, 1978
Delft and Vlaardigen, (The Netherlands)	1980	0.5	--	Guicherit and Schulting, 1985

profiles of acrolein closely followed those of formaldehyde.

No specific measurements of acrolein have been made in California since the late 1960s. Acrolein has often been observed in more recent studies of aldehydes in Los Angeles air (e.g. Grosjean, 1982), but no quantitative data are available due to partial overlap between acrolein and one of its C_3 carbonyl isomers (propanal or acetone, depending upon the analytical conditions employed).

Data for ambient acrolein outside of southern California are very limited. Pellizzari (1978) measured about 2-4 ppb of acrolein in Edison, NJ, at a sampling location heavily influenced by emissions from industrial sources. Guicherit and Schulting (1985) measured acrolein at three locations in the Netherlands (two urban locations and one rural site). About 350 samples were collected at each of the 3 sites. The mean value for 1980 was 0.5 ppb. Minima, maxima and diurnal profiles are probably available, but were not reported or discussed in the peer-reviewed publication (Guicherit and Schulting, 1985).

5.7.2 Condensed Phase Concentrations

There are no reports of acrolein in fog, rainwater or aerosol samples. Acrolein has a high vapor pressure and its presence in urban aerosols is unlikely. Grosjean and Wright (1983) have observed acrolein in southern California rainwater and fogwater samples. No quantitative data were given, again due to incomplete resolution of acrolein from other C_3 carbonyl isomers (propanal or acetone). Acrolein in fog (rain, cloud) may exist as "free" carbonyl, as a bisulfite adduct, or both.

5.8 ATMOSPHERIC CHEMISTRY

5.8.1 In Situ Formation

Acrolein may form in polluted air by reactions of OH and O_3 with 1,3-dienes (CH_2=CH-CH=CHR; R = H: 1,3-butadiene; R = CH_3: 1,3-pentadiene; R = C_2H_5: 1,3-hexadiene; etc.). The corresponding reaction pathways are sum-

summarized in Figure 5.8-1, using 1,3-butadiene as an example. Dienes are highly reactive towards OH ($k \sim 5\text{-}10 \times 10^{-11}$ cm^3 $molecule^{-1}$ sec^{-1}) and ozone ($k \sim 8\text{-}16 \times 10^{-18}$ cm^3 $molecule^{-1}$ sec^{-1}). Ambient concentrations and emission rates of 1,3-dienes are poorly documented. As a result, it is not possible to estimate the importance of in-situ formation of acrolein.

5.8.2 Removal Processes

Acrolein contains two functional groups. As an olefin, it reacts with ozone with a reaction rate constant of about 0.28×10^{-18} cm^3 $molecule^{-1}$ sec^{-1}. As an olefin and as an aldehyde, acrolein reacts with OH with a reaction rate constant of about 1.83×10^{-11} cm^3 $molecule^{-1}$ sec^{-1}. Pathways for the two reactions are given in Figures 5.8-2 and 5.8-3, respectively. The major products of the OH abstraction pathway are formaldehyde (a Level 1 compound) and CO_2; those of the OH addition pathway are formaldehyde and glyoxal; those of the ozone addition are formaldehyde + glyoxylic acid and formic acid + glyoxal. The same reactions may also take place in the liquid phase (e.g. fogwater). Overall, the persistence of acrolein in the atmosphere is expected to be limited by its rapid gas phase reactions with OH and O_3. Photolysis (daytime) and reaction with the nitrate radical (nighttime) represent additional gas phase removal processes for acrolein.

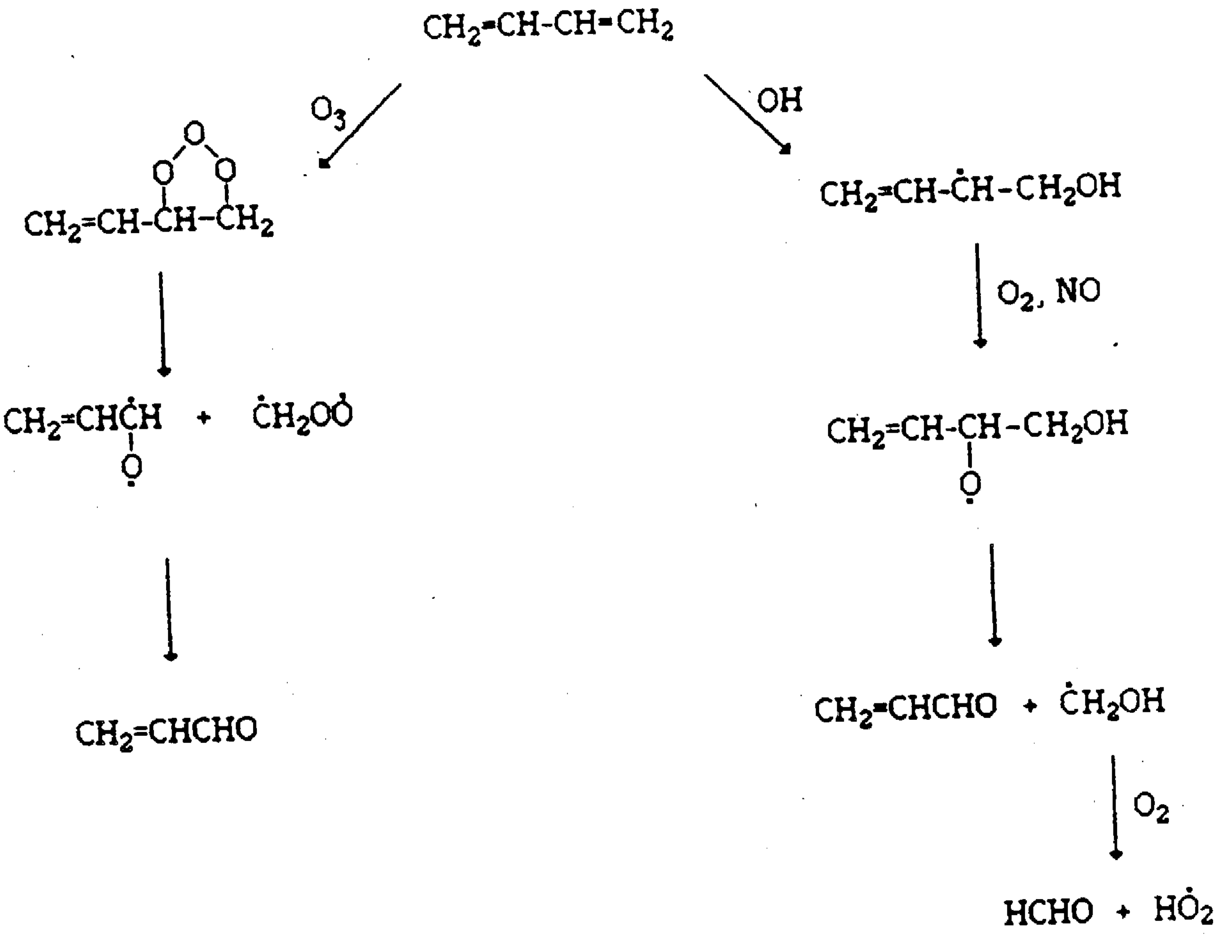


Figure 5.8-1. Formation of Acrolein from 1,3-Dienes.

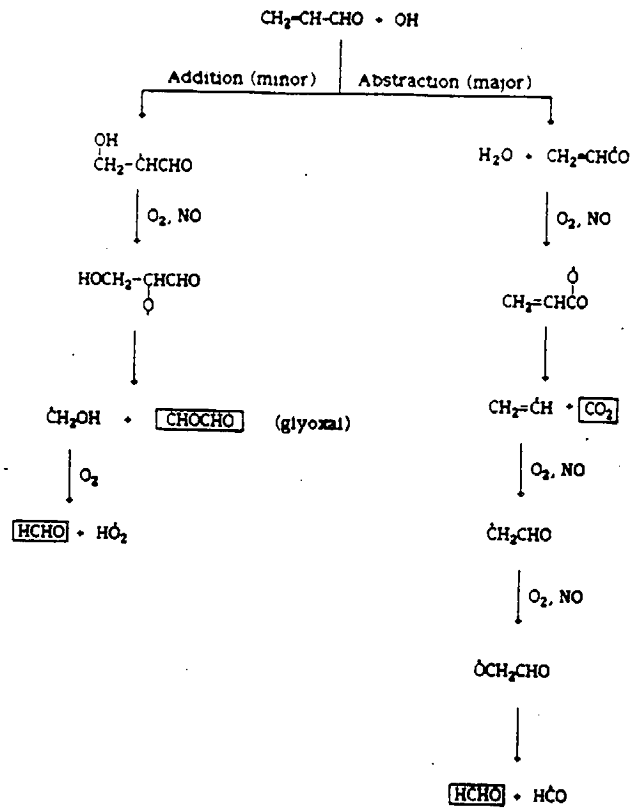


Figure 5.8-2. Reaction of Acrolein with the Hydroxyl Radical.

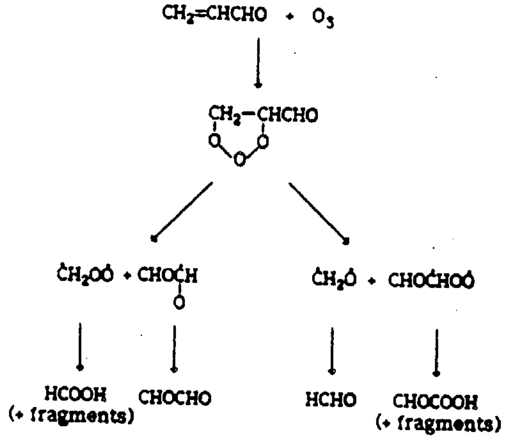


Figure 5.8-3. Reaction of Acrolein with Ozone.

5.9 REFERENCES

Altschuller, A.P. 1983. "Measurements of the products of atmospheric photochemical reactions in laboratory studies and in ambient air. Relationships between ozone and other products," Atmospheric Environment 17:2383-2427.

Altschuller, A.P. and S.P. McPherson. 1963. "Spectrophotometric analysis of aldehydes in the Los Angeles atmosphere," Journal of the Air Pollution Control Association 13:109-111.

Avlani, P. 1986. Personal communication from Associate Air Pollution Specialist, Technical Support Division, California Air Resources Board, Sacramento, CA (6 February).

Barnett, R. 1986. Personal communication from Information Specialist, National Energy Information Center, U.S. Department of Energy, Washington, D.C. (4 June).

Bloomhardt, M.A. and A.S. Pelland. 1985. Source-specific air toxics data for states in EPA Region 9. Prepared by Radian Corporation for U.S. Environmental Protection Agency, Region IX, DCN no. 85-203-024-49-06.

Carey, P. 1981. Mobile source emissions of formaldehyde and other aldehydes. U.S. Environmental Protection Agency, Emission Control Technology Division, Ann Arbor, MI, EPA/AA/CTAB/PA/81-11.

Eimutis, E.C., R.P. Quill, and G.M. Rinaldi. 1978. Source assessment: Noncriteria pollutant emissions (1978 update). Prepared by Monsanto Research Corporation for U.S. Environmental Protection Agency, Industrial Environmental Research Research Laboratory, Research Triangle Park, NC, EPA-600/2-0078-004t.

Gorham, W. 1985. Personal communication from Manager, Safety and Health Affairs, Specialty Chemicals Division, Union Carbide Corporation, Bound Brook, NJ (16 July).

Grosjean, D. 1982. "Formaldehyde and other carbonyls in Los Angeles ambient air," Environmental Science and Technology 16:254-262.

Grosjean, D. and B. Wright. 1983. "Carbonyls in urban fog, ice fog, cloudwater and rainwater," Atmospheric Environment 17:2093-2096.

Guicherit, R. and F.L. Schulting. 1985. "The occurrence of organic chemicals in the atmosphere of the Netherlands," Science of the Total Environment 32:193-219.

Hamilton, J. 1985. Personal communication from Union Carbide Corporation, Danbury, CT (16 July).

Lesh, S.A. and R.C. Mead. 1985. Source screening for acrolein. Prepared by Radian Corporation for U.S. Environmental Protection Agency, Research Triangle Park, NC, Contract No. 68-02-3889.

Lew, V. 1986. Personal communication from Energy Specialist, Biomass Office, Energy Resources, Conservation and Development Commission, Sacramento, CA (9 June).

Lipari, F., J.M. Dasch and W.F. Scruggs. 1984. "Aldehyde emissions from wood-burning fireplaces," Environmental Science and Technology 18(5):326-330.

MVMA (Motor Vehicle Manufacturers Association of the U.S.). 1984. "Motor vehicle facts and figures, 1984," Detroit, MI.

Moran, B. 1986. Personal communication from Assistant President, Tobacco Institute, Washington, D.C. (29 May).

National Research Council, Committee on Aldehydes, Board on Toxicology and Environmental Health Hazards, Assembly of Life Sciences. 1981. Formaldehyde and other aldehydes. National Academy Press, Washington, D.C.

Neumann, H. 1985. Personal communication from Rohm and Haas Company, Philadelphia, PA (12 July).

Pellizzari, E.D. 1978. Measurement of carcinogenic vapors in ambient atmospheres. U.S. Environmental Protection Agency, Research Triangle Park, NC, EPA-600/7-78-062 (NTIS: PB 028 023).

Renzetti, N.A. and R.J. Bryan. 1961. "Atmospheric sampling for aldehydes and eye irritation in Los Angeles smog," Journal of the Air Pollution Control Association 11:421-424.

Rogozen, M., G. Maldonado, D. Grosjean, A. Shochet, and R. Rapoport. 1984. Formaldehyde: a survey of airborne concentrations and sources. Prepared by Science Applications International Corporation for the California Air Resources Board, Sacramento, CA, SAI-84/1642.

SAI (Systems Applications, Inc.). 1980. Human exposure to atmospheric concentration of selected chemicals: Volume I. Prepared for the U.S. Environmental Protection Agency, Research Triangle Park, NC (NTIS: PB81-193252).

Scott Research Laboratories. 1969. Final report on phase 1 atmospheric reaction studies in the Los Angeles Basin. Prepared for Coordinating Research Council (APRAC Project CAPA 7-68) and National Air Pollution Control Administration (CPA 22-69-19).

Sigsby, J., S. Tejada and W. Ray. 1984. Volatile organic compound emissions from 46 in-use passenger cars. U.S. Environmental Protection Agency, Environmental Sciences Research Laboratory, Research Triangle Park, NC.

Stafford, J.K. 1985. Personal communication from Coordinator, Industrial Hygiene/Environmental Affairs, Shell Chemical Company, Dallas, TX (10-16 July).

Sullivan, J.L., F.L. Kafka, and I.M. Ferrari. 1965. "An evaluation of catalytic and direct fired afterburners for coffee and chicory roasting odors," Journal of the Air Pollution Control Association 15(12):583-586.

USEPA (U.S. Environmental Protection Agency). 1976. Compilation of Air Pollutant Emission Factors, Second Edition, Part A. Office of Air and Waste Management, Office of Air Quality Planning and Standards, Research Triangle Park, NC, AP-42.

Verschueren, K. 1977. Handbook of environmental data on organic chemicals. Van Nostrand Reinhold Company, New York, NY.

Warner-Selph, M.A. and H.E. Dietzmann. 1984. Characterization of heavy-duty motor vehicle emissions under transient conditions. Prepared by Southwest Research Institute for U.S. Environmental Protection Agency, Research Triangle Park, NC (NTIS: PB85-124154).

Wood, W. 1986. Personal communication from Fuels Program Specialist, Fossil Fuels Division, California Energy Resources, Conservation and Development Commission, Sacramento, CA (9 June).

6.0

EVALUATION OF ACRYLONITRILE

6.1 PHYSICAL AND CHEMICAL PROPERTIES

Acrylonitrile is a colorless liquid. Table 6.1-1 summarizes some of its physical and chemical properties.

6.2 DIRECT PRODUCTION IN CALIFORNIA

Four manufacturers operated six acrylonitrile plants in the United States in 1977: three in Texas, five in the South and one in Ohio (Key and Hobbs, 1980). To the best of our knowledge, no acrylonitrile production facilities have been built in California since 1977. Therefore, we assume that no acrylonitrile is emitted from direct production in the state.

6.3 INDIRECT PRODUCTION AND EMISSIONS IN CALIFORNIA

As mentioned in Section 6.8, there is no known atmospheric reaction leading to acrylonitrile. Furthermore, we can locate no literature indicating any indirect production of acrylonitrile.

6.4 INDUSTRIAL USE AND EMISSIONS

In 1983 acrylonitrile was used as a comonomer for acrylic and modacrylic fibers (51 percent), for acrylonitrile-butadiene-styrene (ABS) resins (18 percent), for nitrile elastomers (3 percent), for styrene-acrylonitrile resins (2 percent), and as a chemical intermediate in the manufacture of adiponitrile (13 percent), and acrylamide (6 percent) (SRI, 1983). In late 1985, U.S. acrylonitrile plants were operating at or close to capacity but domestic demand was flat or declining; the only growth in the market for acrylonitrile was in exports (Agoos et al., 1985). Acrylonitrile, produced at the domestic plants mentioned in Section 6.2, is primarily used captively in the production of the aforementioned fibers and resins. Acrylonitrile

Table 6.1-1

CHEMICAL DATA SUMMARY FOR ACRYLONITRILE

Property	Value for Acrylonitrile
CAS Registry No.	107-13-1
Synonyms	propenenitrile, vinyl cyanide
Molecular Weight	53.06
Molecular Formula	C_3H_3N
Molecular Structure	CH_2=CH-CN
Physical State at STP	Colorless liquid
Boiling Point	77.3°C
Melting Point	-83°C
Specific Gravity	0.8004 at 25°C
Vapor Pressure	
20°C	83 mm Hg
30°C	137 mm Hg
Vapor Density (air=1)	1.83
Solubility	7.3% by weight in all common organic solvents
Log Partition Coefficient (octanol/H_2O)	0.25
Henry's Law Constant	0.0884 atm-L/mole

Source: SAI (1980); Verschueren (1977), ICF (1985).

does not appear to be used in the manufacture of these products in California.

Acrylonitrile is used by Rohm and Haas California, Inc. in Hayward as a feedstock for six grades of water-based acrylic polymer resins. During 1984 and 1985, Rohm and Haas used 168,000 lb and 308,000 lb of acrylonitrile, respectively (Henderson, 1986). According to the Bay Area Air Quality Management District (BAAQMD), only trace amounts of the compound were emitted by the Hayward Plant (Hill, 1985). Acrylonitrile is used by the Dow Chemical Company to make ABS resins at its plant in Torrance (Cox, 1986). The South Coast Air Quality Management District (SCAQMD) reports that approximately 2 tons/yr are emitted by the Torrance plant (Zwiacher, 1983). A recent inventory prepared for U.S. Environmental Protection Agency Region IX, however, estimated only 440 lb/yr for this plant (Bloomhardt and Pelland, 1985).

As seen in Table 6.4-1, only three facilities in the SCAQMD and BAAQMD toxic emission inventories, Dow Chemical Company, Genentech, and Fuller O'Brien, are reported to have significant emissions. The manager of the health and safety department at Genentech told SAIC that his company used acrylonitrile in experiments, but would not elaborate (Palchek, 1986). He indicated further that he had spoken with Steve Hill of the BAAQMD on numerous occasions about having the company removed from the BAAQMD emission inventory because of the inaccuracy of the reported emissions of 1,400 lb/yr. Fuller-O'Brien stated that acrylonitrile was used to produce resins. Their estimated annual emissions are 200 lb (Hill, 1985).

Table 6.4-2 shows users of acrylonitrile who appear on the carcinogen registration list of the Division of Occupational Safety and Health, California Department of Industrial Relations. The three firms who are also reported by the BAAQMD, SCAQMD, or EPA, and are therefore listed in Table 6.4-1, are identified with asterisks. Neither the amount of use nor the quantity of emissions from these facilities is known. The reason why the AQMD emission inventories and the carcinogen registry have so few facilities in common is also unknown. One possibility is that the air quality management districts have not been informed about the use of acrylonitrile by these firms. A second possibility is that emissions are near zero and therefore not reported.

Table 6.4-1

REPORTED ACRYLONITRILE EMITTERS IN CALIFORNIA

Firm	City	County	SCAQMD lb/yr	SCAQMD kg/yr	BAAQMD lb/yr	BAAQMD kg/yr	EPA Region IX lb/yr	EPA Region IX kg/yr
Ace Rubber Company	South Gate	Los Angeles	1	0.5	-	-	-	-
AiResearch Div. of Garret Corp.	Torrance	Los Angeles	1	0.5	-	-	-	-
All West Plastics, Inc.	Huntington Beach	Orange	1	0.5	-	-	-	-
Applied Plastics Co., Inc.	El Segundo	Los Angeles	1	0.5	-	-	-	-
Custom Rubber Mix, Inc.	Los Angeles	Los Angeles	42	19.0	-	-	-	-
DOE Sandia National Lab	Livermore	Alameda			T[a]			
Dow Chemical U.S.A	Torrance	Los Angeles	4,000	1,814.1	-	-	440	200
ESCO Rubber Products, Inc.	Brea	Orange	13	5.9	-	-	-	-
Fuller-O'Brien	So. San Francisco	San Mateo			200	91		
Genentech, Inc.	So. San Francisco	San Mateo			1,400	630		
Golden State Rubber and Latex Corp.	Gardena	Los Angeles	1	0.5	-	-	-	-
IT Corp, Oil Reprocessing	Martinez	Contra Costa			U[a]			
Kaiser Aluminum & Chemical	Pleansanton	Alameda			T			
Kresky Signs, Inc.	Petaluma	Sonoma			T			
Lawrence Livermore National Lab.	Livermore	Alameda			T			
Master Processing Corp.	Long Beach	Los Angeles	1	0.5	-	-	-	-
Miracle Auto Painting	Concord	Contra Costa			T			
Miracle Auto Painting	Sunnyvale	Santa Clara			T			
Polyvinyl Chemical Industr.	Vallejo	Solano			T			
R & G Sloane Manufacturing, Inc.	Sun Valley	Los Angeles	1	0.5	-	-	-	-
Rohm and Haas California	Hayward	Alameda			T			
Rohr Industries, Inc.	Riverside	Riverside	1	0.5	-	-	-	-
Rubber-Teck, Inc.	Gardena	Los Angeles	1	0.5	-	-	-	-
Rubbercraft Corp. of California	Torrance	Los Angeles	1	0.5	-	-	-	-
Sherex Chemical Company	Oakland	Alameda			T			
Trojan Battery Company	Santa Fe Springs	Los Angeles	1	0.5	-	-	-	-
Union Carbide Corp.	Torrance	Los Angeles	1	0.5	-	-	-	-
Union Oil Company, S/T Division	Brea	Orange	1	0.5	-	-	-	-
United Technologies	San Jose	Santa Clara			T			
Varian Associates Corp.	Palo Alto	Santa Clara			T			
Totals			4,068	1,845	1,600	730	440	200

Source: Summarized from emissions reported by the South Coast Air Quality Management District (Zwiacher et al., 1983), the Bay Area Air Quality Management District (Hill, 1985) and the U.S. Environmental Protection Agency (Bloomhardt and Pelland, 1985).

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

Table 6.4-2
ACRYLONITRILE USERS FROM THE OCCU CARCINOGEN REGISTRATION LIST[a]

Firm	City	County	Firm	City	County
Aerojet Strategic Propulsion	Sacramento	Sacramento	IT Corp.	Rio Vista	Solano
American Environmental Corp.	Rancho Cordova	Sacramento	IT Corp.	Westmorland	Imperial
Analytical Research Labs Inc.	Monrovia	Los Angeles	IT Corp.	Benicia	Solano
Aerojet Tech Systems	Sacramento	Sacramento	IT Corp.	Irvine	Orange
Beckman Industrial Corp.	Fullerton	Orange	IT Corp.	Martinez	Contra Costa
Beckman Instruments Inc.	Fullerton	Orange	IT Corp.	Cerritos	Los Angeles
BKK Corporation	Torrance	Los Angeles	IT Corp.	Martinez	Contra Costa
Calif. Institute of Technology	Pasadena	Los Angeles	IT Corp.	Santa Clara	Santa Clara
California Bionuclear Corp.	Sun Valley	Los Angeles	IT Corp.	Walnut Creek	Contra Costa
California Water Labs Inc.	Modesto	Stanislaus	J H Kleinfelder & Associates	Walnut Creek	Contra Costa
Canonie Engineers	Stockton	Contra Costa	Jorco Chemical Company	Redlands	San Bernardino
Chemical Waste Management	Anaheim	Orange	Kamtec	Walnut Creek	Contra Costa
Chemical Waste Management	Kettleman	Kings	Microsensor Technology Inc.	Fremont	Alameda
Chemical Waste Management	Coalinga	Fresno	Montgomery Laboratories	Pasadena	Los Angeles
Chevron Chemical Co.	Richmond	Marin	Polyvinyl Chemical Industries	Vallejo	Solano
Chevron Oil Field Research Co.	La Habra	Orange	Rancho Santiago Community College	Santa Ana	Orange
Chevron Research	Richmond	Marin	*Rohm and Haas California Inc.	Hayward	Alameda
City of LA Dept. of Public Works	Playa Del Rey	Los Angeles	Rohm and Haas California Inc.	Redwood City	San Mateo
City of LA Dept. of Public Works	Van Nuys	Los Angeles	S-Cubed	La Jolla	San Diego
City of Santa Barbara	Santa Barbara	Santa Barbara	Safety Specialists Inc.	Santa Clara	Santa Clara
College of Marin	Kentfield	Marin	Sampson Environmental	Long Beach	Los Angeles
Conductimer	San Jose	Santa Clara	SRI International	Menlo Park	San Mateo
Cratex Manufacturing	Benicia	Solano	State of California	Los Angeles	Los Angeles
Crosby & Overton Inc.	Long Beach	Los Angeles	Stauffer Chemical Company	Richmond	Marin
EAL Corp.	Richmond	Marin	The Aerospace Corporation	El Segundo	Los Angeles
Environmental Protection Corp.	Bakersfield	Kern	The O'Brien Corporation	So. San Francisco	San Mateo
Fortin Laminating Corp.	Pacoima	Los Angeles	Union Carbide Chemicals & Plastics	Torrance	Los Angeles
General Tire & Rubber Co.	Orange	Orange	*Union Carbide Corporation	Torrance	Los Angeles
Hexcel	El Segundo	Los Angeles	Union Oil Company of California	La Mirada	Los Angeles
Hughes Aircraft Co.	El Segundo	Los Angeles	Union Science & Technology	Brea	Orange
Industrial Waste Engineering	Long Beach	Los Angeles	United Technologies Corp/Csd.	San Jose	Santa Clara
IT Corp.	Martinez	Contra Costa	UC San Francisco	San Francisco	San Mateo
IT Corp.	Wilmington	Los Angeles	UC Berkeley	Berkeley	Alameda
IT Corp.	Torrance	Los Angeles	UC Riverside	Riverside	Riverside
IT Corp.	San Diego	San Diego	USC	Los Angeles	Los Angeles
IT Corp.	Martinez	Contra Costa	Varian Associates-Instruments Dept.	Walnut Creek	Contra Costa
IT Corp.	San Jose	Santa Clara	Western Colloid Products	Oakland	Alameda
IT Corp.	Wilmington	Los Angeles	Zoecon Corporation	Palo Alto	Santa Clara
IT Corp.	Taft	Kern	ZWS (Zero Waste Systems Inc.)	Oakland	Alameda
IT Corp.	Benicia	Solano			
*IT Corp.	Martinez	Contra Costa			

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[a] Amount of use or emissions not reported
*Firm listed in Table 6.4-1

6.5 CONSUMER USE AND EMISSIONS

According to the Stanford Research Institute (SRI, 1983), no consumer use for acrylonitrile appears to exist; therefore, a reasonable assumption is that acrylonitrile is not volatilized from consumer products. However, we have no information on whether acrylonitrile is trapped within the finished ABS resin matrix and slowly released from the plastics which such resins comprise.

6.6 EMISSION SUMMARY

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 of acrylonitrile are emitted from use of the compound as an ingredient in resins. Given conflicting estimates for two of the plants, the statewide total may be as low as 0.4 tons; hence there is considerable uncertainty in the total. There are not likely to be releases of acrylonitrile from consumer products, nor are there any known indirect formation pathways for the production of the compound.

6.7 SUMMARY OF AMBIENT CONCENTRATION DATA

6.7.1 Gas Phase Concentrations

No data are available for acrylonitrile in California. Going (1978) collected 1 - 8 samples each at 12 source-dominated sites in other states, for a total of 43 samples. The mean acrylonitrile concentration was 12 ppb, and the maximum level recorded was 110 ppb. To our knowledge, there is no other report available regarding ambient acrylonitrile concentrations, in the U.S. or elsewhere.

6.7.2 Condensed Phase Concentrations

No data are available for condensed phase acrylonitrile. Acrylonitrile has a high vapor pressure and is not expected to condense as aerosol. The compound is also poorly soluble, and is not expected to be abundant in rain, fog or cloudwater.

6.8 ATMOSPHERIC CHEMISTRY

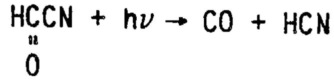
6.8.1 In-Situ Formation

There is no known reaction that would lead to in-situ formation of nitriles, including acrylonitrile, in the atmosphere.

6.8.2 Removal Processes

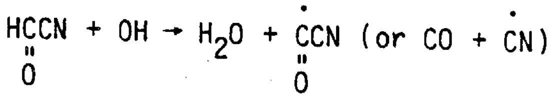
Acrylonitrile, once emitted into the atmosphere, is expected to be long-lived in view of its low reactivity towards OH, O_3, and NO_3 (reaction rate constants of 5×10^{-12}, 1×10^{-19} and 6×10^{-18} cm^3 $molecule^{-1}$ sec^{-1}, respectively). The photolysis rate of acrylonitrile in sunlight has not been measured, but is presumably negligibly slow by analogy to that of its structural homologue acetonitrile (CH_3CN). Again by analogy with acetonitrile (Snider and Dawson, 1985), acrylonitrile is expected to be stable against oxidation in the aqueous phase.

The reaction of OH with acrylonitrile has been investigated by Hashimoto et al. (1984). Formaldehyde and formyl cyanide, $H\underset{\overset{\|}{O}}{C}CN$, are the major reaction products. The corresponding reaction pathways are shown in Figure 6.8-1. The reaction mechanism was supported by similar findings for the reaction of OH with two other unsaturated nitriles, allyl cyanide and methacrylonitrile, $CH_2 = CHCH_2CN$ and $CH_2 = C(CH_3)CN$ (Hashimoto et al., 1984). The fate of the reaction product formyl cyanide was not investigated in detail. It presumably photolyzes to form hydrogen cyanide and carbon monoxide:



$$H\underset{\overset{\|}{O}}{C}CN + h\nu \rightarrow CO + HCN$$

or reacts (slowly) with OH:



$$H\underset{\overset{\|}{O}}{C}CN + OH \rightarrow H_2O + \underset{\overset{\|}{O}}{\dot{C}}CN \text{ (or } CO + \dot{C}N\text{)}$$

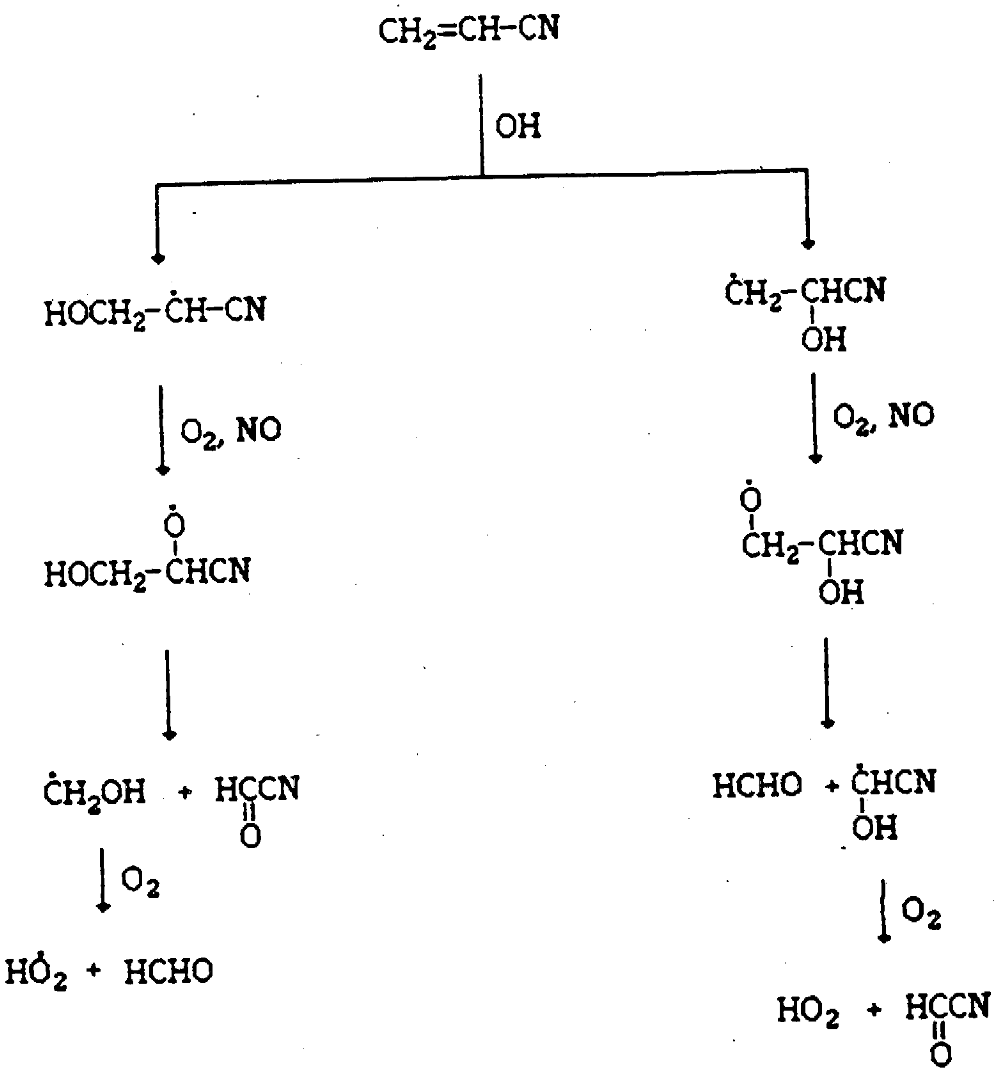


Figure 6.8-1. Reaction of OH with Acrylonitrile.

Indeed, small amounts of HCN, along with HCHO and HCOCN, were formed in the acrylonitrile-OH-NO experiments of Hashimoto et al. (1984).

6.9 REFERENCES

Agoos, A., P. Savage and S. Ushia. 1985. "Acrylonitrile demand shifts overseas," Chemical Week 137(23):18-20.

Bloomhardt, M.A. and A.S. Pelland. 1985. Source-specific air toxics data for states in EPA Region 9. Prepared by Radian Corporation for U.S. Environmental Protection Agency, Region IX, DCN no. 85-203-024-49-06.

Cox, T. 1986. Personal communication from Environmental Control Division, Dow Chemical Company, Torrance, CA (20 August).

Going, J.E. 1978. Environmental monitoring near industrial sites: acrylonitrile. Midwest Research Institute, Kansas City, MO (NTIS: PB 295 928).

Hashimoto, S., H. Bandow, H. Akimoto, J.H. Weng and X.Y. Tang. 1984. "Products and mechanisms for the OH radical initiated oxidation of acrylonitrile, methacrylonitrile and allyl cyanide in the presence of NO," International Journal of Chemical Kinetics 16:1385-1399.

Henderson, C. 1986. Letter from Environmental Manager, Rohm and Haas California, Inc. Hayward, CA (18 February).

Hill, S. 1985. 1984 toxic use survey: Bay Area Air Quality Management District. Bay Area Air Quality Management District, San Francisco, CA.

ICF (ICF Incorporated). 1985. Draft Superfund public health evaluation manual. Prepared for the U.S. Environmental Protection Agency, Office of Emergency and Remedial Response, Office of Solid Waste and Emergency Response, Washington DC, Appendix C-1

Key, J. and F. Hobbs. 1980. "Acrylonitrile," in Organic chemical manufacturing volume 10: selected processes. Prepared by IT Enviroscience for Office of Air Quality Planning and Standards, Environmental Protection Agency, Research Triangle Park, NC.

Palchek, R. 1986. Personal communication from Manager of Health and Safety, Genentech, Inc., San Francisco, CA (20 August).

SAI (Systems Applications, Inc.). 1980. Human exposure to atmospheric concentration of selected chemicals: Volume I. Prepared for the U.S. Environmental Protection Agency, Research Triangle Park, NC (NTIS: PB81-193252).

Snider, J.R. and G.A. Dawson. 1985. "Tropospheric light alcohols, carbonyls and acetonitrile: concentrations in the southwestern United States and Henry's law data," J. Geophys. Res. 90:3797-3805.

SRI (Stanford Research Institute). 1983. 1983 Directory of chemical producers, United States of America. SRI International, Menlo Park, CA.

Verschueren, K. 1977. Handbook of environmental data on organic chemicals. Van Nostrand Reinhold Company, New York, NY.

Zwiacher, W.E., L.D. Yuhas, J.S. Fakhoury, J.L. Whittaker, and J. Grisinger. 1983. Emissions of potentially toxic/hazardous air contaminants in the South Coast Air Basin. South Coast Air Quality Management District, Engineering Division, El Monte, CA.

7.0

EVALUATION OF ALLYL CHLORIDE

7.1 PHYSICAL AND CHEMICAL PROPERTIES

Allyl Chloride is a colorless to pale yellow liquid. Table 7.1-1 summarizes some of its physical and chemical properties.

7.2 DIRECT PRODUCTION IN CALIFORNIA

There are only two U.S. producers of allyl chloride, neither of which is in California (Panzarella, 1985; Stehr, 1985).

7.3 INDIRECT PRODUCTION AND EMISSIONS IN CALIFORNIA

Allyl chloride is not known to be a byproduct of any manufacturing process in California, and it is not a combustion product. Therefore no emissions of this type are likely.

7.4 INDUSTRIAL USE AND EMISSIONS

Allyl chloride is used in very small quantities (approximately 500 lb per year) as a "reactant" in the manufacture of phenol-formaldehyde resins by at least one company, Specialty Organics, located in Irwindale (McAuley, 1985). Emission factors for this pollutant in phenol-formaldehyde manufacturing are unavailable. Indeed, allyl chloride is not mentioned in an extensive description of phenolic resin production processes by Wilkins (1977). Formica (1978) reports that total uncontrolled VOC emissions from phenol-formaldehyde processes are 7.5 lb/ton of product. However, as we are unable to relate allyl chloride use to product mass, we can only estimate an upper bound of 500 lb/yr emissions in California.

7.5 CONSUMER USE AND EMISSIONS

According to the Toxicology Data Base, allyl chloride is used solely as an intermediate in the manufacture of various chemicals; none is directly

Table 7.1-1

CHEMICAL DATA SUMMARY FOR ALLYL CHLORIDE

Property	Value for Allyl Chloride
CAS Registry No.	107-05-1
Synonyms	3-chloroprene, AC, Chlorallylene, 3-chloro-1-propene, 1-chloro-2-propene, 3-chloropropylene
Molecular Weight	76.53
Molecular Formula	C_3H_5Cl
Molecular Structure	$CH_2 = CH - CH_2Cl$
Physical State at STP	Colorless to pale yellow liquid[a]
Boiling Point	44.6°C
Melting Point	-134.5°C
Specific Gravity	0.938 at 20°C/4°C
Vapor Pressure	359 mm at 25°C
Vapor Density (air=1)	2.64
Solubility	Soluble (33 g/L of H_2O at 20°C)
Log Partition Coefficient (octanol/H_2O)	
Henry's Law Constant	

Source: SAI (1980) unless otherwise noted.

[a] Verschueren (1977).

used in consumer products. Therefore, there are no emissions of allyl chloride to the ambient air from consumer products.

7.6 EMISSION SUMMARY

The only potential source of allyl chloride emissions in California is from manufacture of phenol-formaldehyde resins at one location in Los Angeles County. Our emission estimate of less than 0.25 ton (0.23 kkg) per year is highly uncertain.

7.7 SUMMARY OF AMBIENT CONCENTRATION DATA

To our knowledge, there are no data regarding ambient concentrations of allyl chloride, in California or elsewhere.

7.8 ATMOSPHERIC CHEMISTRY

7.8.1 In-Situ formation

There are no known reactions that could lead to the in-situ production of allyl chloride in the atmosphere.

7.8.2 Removal Processes

No information is available regarding the rates of reactions of allyl chloride with ozone, the hydroxyl radical, or the nitrate radical. Rate constants we estimated from structure-reactivity relationships (see Section 3.2.2) are $k_{OH} = 1.7 \times 10^{-11}$, $k_{O_3} = 3.6 \times 10^{-18}$, and $k_{NO_3} = 8.2 \times 10^{-16}$ cm^3 $molecule^{-1}$ sec^{-1}. These estimated rate constants suggest that the atmospheric persistence of allyl chloride will be limited by its reaction with OH and, to a lesser extent, with ozone and with NO_3.

The reaction of allyl chloride with OH has been the object of only one recent experimental study (Shepson et al., 1986). The major products were formaldehyde (a Level 1 compound) and chloroacetaldehyde. These findings are consistent with the overall mechanism shown in Figure 7.8-1, which describes

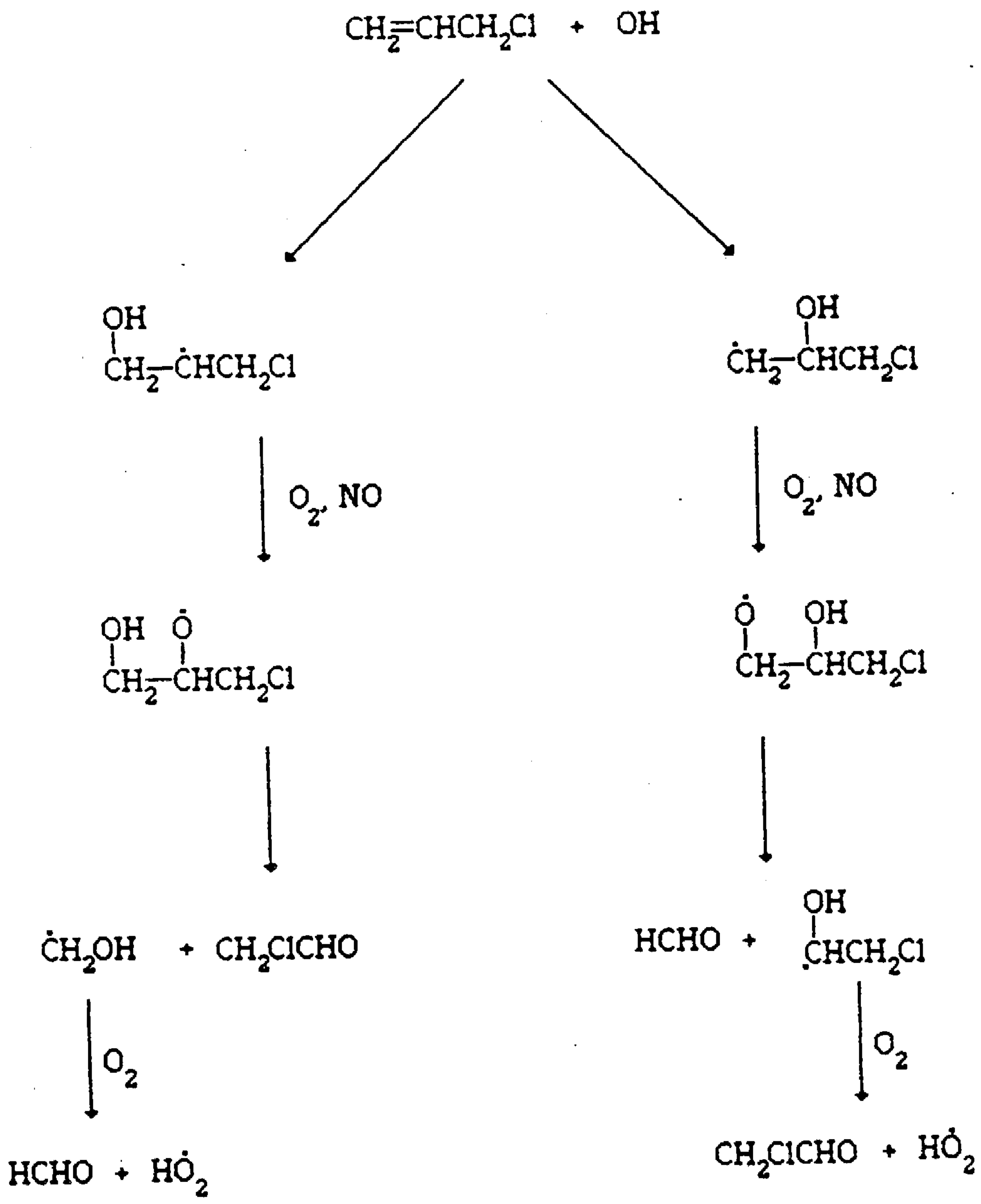
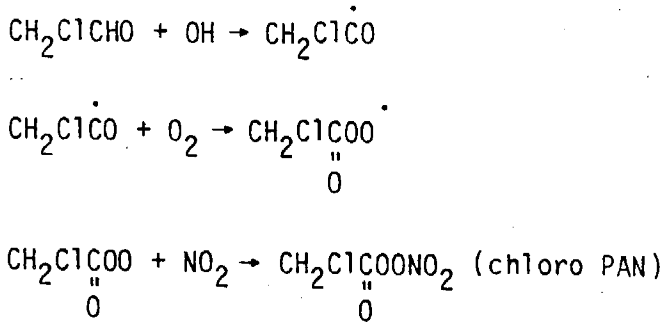


Figure 7.8-1. Reaction of OH With Allyl Chloride.

the reaction of OH with $CH_2=CHCH_2X$ compounds including X = H (propene), X = Cl (allyl chloride), and X = CN (allyl cyanide), and is supported by the corresponding experimental studies of reaction products (Shepson et al., 1986; Hashimoto et al., 1984).

With chloroacetaldehyde as a major reaction product, photooxidation of allyl chloride-NO_x mixtures is expected to yield some chloroperoxyacetyl nitrate (chloro-PAN):



$$\mathrm{CH_2ClCHO + OH \rightarrow CH_2Cl\dot{C}O}$$

$$\mathrm{CH_2Cl\dot{C}O + O_2 \rightarrow CH_2Cl\underset{\overset{\|}{O}}{C}OO^{\bullet}}$$

$$\mathrm{CH_2Cl\underset{\overset{\|}{O}}{C}OO + NO_2 \rightarrow CH_2Cl\underset{\overset{\|}{O}}{C}OONO_2}\ \text{(chloro PAN)}$$

as was indeed observed by Shepson et al. (1986). Shepson et al. also reported that the photooxidation products of allyl chloride were highly mutagenic, as tested with the Ames bioassay, and that chloro-PAN accounted for some, but not all, of the observed mutagenicity.

The reaction of ozone with allyl chloride has not been studied. A tentative mechanism, based upon that for the reaction of O_3 with propene, is shown in Figure 7.8-2. Expected major products are formaldehyde, formic acid, chloroacetaldehyde, and chloroacetic acid.

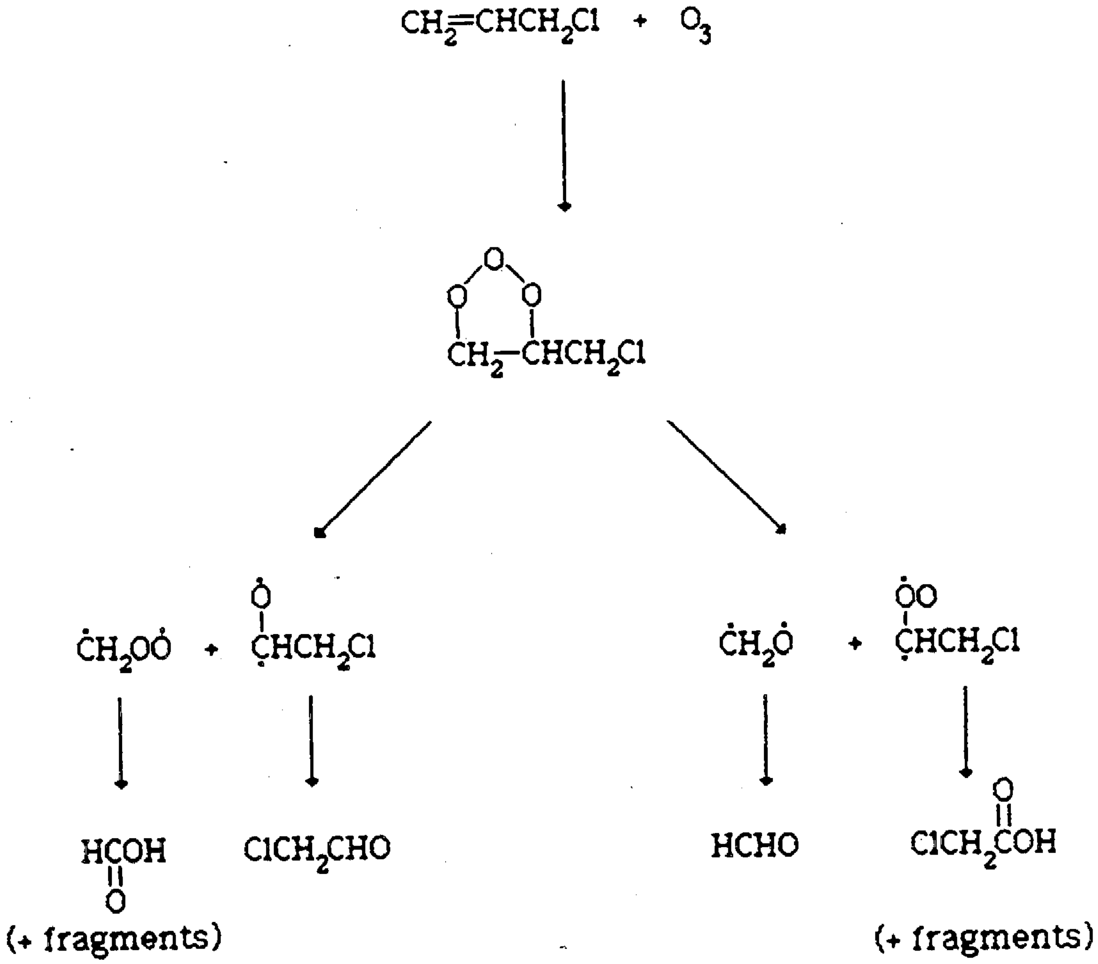


Figure 7.8-2. Reaction of Ozone With Allyl Chloride.

7.9 REFERENCES

Formica, P.N. 1978. Controlled and uncontrolled emission rates and applicable limitations for eighty processes. Prepared by TRC for the U.S. Environmental Protection Agency, Research Triangle Park, NC, EPA-450/2-77-016 (NTIS: PB 266 978).

Hashimoto, S., H. Bandov, H. Akimoto, J.H. Weng and X.Y. Tang. 1984. "Products and mechanism for the OH radical initiated oxidation of acrylonitrile and allyl cyanide in the presence of NO," International Journal of Chemical Kinetics 16:1385-1399.

McAuley, D. 1985. Personal communication from Business Manager, Specialty Organics, Inc., Irwindale, CA.

Panzarella, J. 1985. Personal communication from Production Specialist, Dow Chemical Company, Freeport, TX (16 July).

SAI (Systems Applications, Inc.). 1980. Human exposure to atmospheric concentration of selected chemicals: Volume 2. Prepared for the U.S. Environmental Protection Agency, Research Triangle Park, NC (NTIS: PB81-193252).

Shepson, P.B., T.E. Kleindienst, E.O. Edney and C.M. Nero. 1986. "The mutagenic activity of the products of the photooxidation of allyl chloride." Paper presented at the 192nd National Meeting of the American Chemical Society, Division of Environmental Chemistry, Anaheim, CA (8-12 September).

Stehr, C.E. 1985. Personal communication from Celanese Chemical Company, Houston, TX (10 July).

Verschueren, K. 1977. Handbook of environmental data on organic chemicals. Van Nostrand Reinhold Company, New York, NY.

Wilkins, G.E. 1977. Industrial process profiles for environmental use: Chapter 10. Plastics and resins industry. Prepared by Radian Corporation for the U.S. Environmental Protection Agency, EPA-600/2-77-023j

8.0

EVALUATION OF BENZYL CHLORIDE

8.1 PHYSICAL AND CHEMICAL PROPERTIES

Benzyl chloride is a very refractive liquid. Table 8.1-1 summarizes some of its physical and chemical properties.

8.2 DIRECT PRODUCTION

The two primary producers of benzyl chloride are Monsanto Polymer Products Company and Stauffer Chemical Company. Neither company produces benzyl chloride in California (Farley, 1985; Mamola, 1985; Sommer, 1985).

8.3 INDIRECT PRODUCTION AND EMISSIONS IN CALIFORNIA

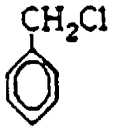
As mentioned in Section 8.8, there are no known reactions that could cause the in-situ formation of benzyl chloride in the atmosphere. No other indirect mechanisms are presently known for the production of benzyl chloride.

8.4 INDUSTRIAL USE AND EMISSIONS

Ten percent of U.S. benzyl chloride production is used for manufacturing quaternary ammonium salts, which are in turn components of various consumer products such as hair sprays (Farley, 1985; Mamola, 1985; Sommer, 1985). Six percent is used in the manufacture of benzyl alcohol, and another six percent of production goes toward miscellaneous other uses, such as the manufacture of penicillin, benzyl esters, triphenylmethane dyes, rubber accelerators, gasoline gum inhibitors, pickling inhibitors, synthetic tannins, and dibenzyl disulfide. Whether any of these uses occur in California is uncertain. Monsanto, one of the two manufacturers of benzyl chloride, does not use the chemical in California. Stauffer Chemical Company representatives we contacted stated that the firm ships it to California, where it is used in the production of quaternary ammonia compounds. However, one manufacturer we contacted stated that no benzyl chloride is used on the West Coast for this

Table 8.1-1

CHEMICAL DATA SUMMARY FOR BENZYL CHLORIDE

Property	Value for Benzyl Chloride
CAS Registry No.	100-44-7
Synonyms	α-tolylchloride, chloromethylbenzene, α-chlorotoluene
Molecular Weight	126.59
Molecular Formula	C_7H_7Cl
Molecular Structure	
Physical State at STP	Liquid - very refractive
Boiling Point	179°C at 760 mm
Melting Point	-39°C
Specific Gravity	1.1026 at 18°C/4°C
Vapor Pressure	1.4 mm at 25°C
Vapor Density (air=1)	4.36
Solubility	Insoluble (H_2O)
Log Partition Coefficient (octanol/H_2O)[a]	2.63
Henry's Law Constant[a]	0.0506 atm-L/mole

Source: SAI (1980), unless otherwise noted.

[a] ICF (1985).

purpose (Lane, 1986).

About 72 percent of the production of benzyl chloride is used as a chemical intermediate in the manufacture of benzyl phthalate plasticizers, including butyl benzyl phthalate (BBP) (60 percent) (SRI, 1981). No benzyl phthalate plasticizers are manufactured in California (Perwak et al., 1981). However, some benzyl chloride apparently remains in the plasticizers as a contaminant, so that when the plasticizers are added to other materials, benzyl chloride could be released. According to Gledhill et al. (1980) and Perwak et al. (1981), the chief use of butyl benzyl phthalate is as a plasticizer for PVC floor tiles. In a study performed in Sweden by Sandberg et al. (1984), benzyl chloride was released during the manufacture of PVC floor tiles which contained butyl benzyl phthalate. A workspace concentration of 0.03 mg/m^3 was measured.

To explore the potential for release of benzyl chloride in PVC manufacturing, we contacted 13 U.S. PVC manufacturers whose names were reported in the Chemicalweek Buyers' Guide '86 (McCurdy, 1985) and the Society of the Plastics Industry, Inc. 1980 Membership Directory and Buyers Guide (SPI, 1980). Five of these firms were in California. Only one of these companies (Monsanto in St. Louis, Missouri) uses BBP in PVC resins. One manufacturer told SAIC that the volatility of benzyl phthalate is too high; users prefer that the plasticizer remain in the PVC for a longer time.

Table 8.4-1 shows the results of a Bay Area Air Quality Management District inventory of benzyl chloride in its jurisdiction (Hill, 1985). The 4 tons/year estimate for the Sunnyvale Air Force Station turned out to be incorrect; the survey respondent actually uses an ammonium salt (Smith, 1987).

8.5 CONSUMER USE AND EMISSIONS

A search of current literature and formulary references did not reveal any consumer products in which benzyl chloride is used directly. Derivatives of benzyl chloride are, however, used extensively in industrial and consumer products. This does not preclude the possibility that benzyl chloride may be found in trace quantities in certain consumer products.

Table 8.4-1

BENZYL CHLORIDE EMISSIONS IN THE SAN FRANCISCO BAY AREA

Source	City	Emissions (tons/yr)
Alameda County		
Clorox Technical Center	Pleasanton	U[a]
Lawrence Livermore National Laboratory	Livermore	T[a]
Contra Costa County		
Chevron Research Company	Richmond	T
San Mateo County		
SRI International	Menlo Park	T
Santa Clara County		
Sunnyvale Air Force Station	Sunnyvale	4.0[b]
Sonoma County		
Hewlett-Packard Company	Santa Rosa	T
Kresky Signs, Inc.	Petaluma	T

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

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

[b] This estimate later found to be incorrect; no benzyl chloride is used at this facility (Smith, 1987).

As was noted in Section 8.4, benzyl chloride is a contaminant in butyl benzyl phthalate, which is used as a plasticizer in certain polyvinyl chloride (PVC) products, for example, PVC floor tiles. Apparently, outgassing from floor tiles continues for a considerable time after the tiles are laid. Sandberg et al. (1984) report a "half life" of benzyl chloride in floor tiles of about 100 days. In addition, significant quantities of BBP (and, presumably, benzyl chloride) are present in rubber gloves and polyvinyl acetate-based caulking and adhesives (Felder, 1985). The potential for emissions from use of these is unknown.

8.6 EMISSION SUMMARY

No direct production of benzyl chloride takes place in California. Benzyl chloride is used in the production of benzyl phthalate plasticizers, which are used to some extent in PVC products. Some outgassing from benzyl chloride trapped as a contaminant might occur. Whether the compound is used in California to manufacture quaternary ammonium compounds for various consumer products, such as hair sprays is uncertain. Several other derivatives of benzyl chloride are used in consumer products. Benzyl chloride might be a contaminant, resulting in small releases from these products. Emissions in the San Francisco Bay Area may be about 1 ton/yr, although the processes of release are unknown.

8.7 SUMMARY OF AMBIENT CONCENTRATION DATA

No literature data could be found regarding ambient concentrations of benzyl chloride, in California or elsewhere.

8.8 ATMOSPHERIC CHEMISTRY

8.8.1 In-Situ Formation

There are no known reactions that could lead to in-situ formation of benzyl chloride in the atmosphere.

8.8.2 Removal Processes

There are essentially no data regarding removal processes for atmospheric benzyl chloride. Photolysis, reaction with ozone ($k \leq 4 \times 10^{-20}$ cm^3 $molecule^{-1}$ sec^{-1}) and reaction with the nitrate radical are negligible, as are scavenging by hydrometeors and subsequent aqueous phase reactions. Reaction with OH appears to be the dominant loss process, with a reaction rate constant (estimated from structure reactivity relationship) of 1.3×10^{-12} cm^3 $molecule^{-1}$ sec^{-1}.

The benzyl chloride-OH reaction has not been studied experimentally. A tentative reaction mechanism is given in Figure 8.8-1. This mechanism is identical to that of the reaction of OH with toluene, which has been studied in great detail (e.g. Leone and Seinfeld, 1984; Leone et al., 1985; Gery et al., 1985; and references therein). The reaction of OH with toluene involves two pathways. Addition on the aromatic ring is the major pathway at ambient temperature, accounting for about 90 percent of the total reaction. The OH adduct then reacts with NO_2 to give nitrotoluenes, and with O_2 to yield cresols and ring-opening aliphatic carbonyls. The abstraction pathway leads to benzaldehyde and its reaction products, including peroxybenzoyl nitrate, PBzN (e.g. Grosjean, 1985). The major uncertainties in the OH-toluene reaction mechanism are (1) the relative yields of "ring-conserving" (cresols, etc.) vs "ring opening" (aliphatic carbonyls) products, and (2) the nature, relative abundance and further reactions of the aliphatic carbonyls.

Application of the toluene-OH reaction mechanism to the benzyl chloride-OH reaction, as is shown in Figure 8.8-1, leads to the following reaction products. The abstraction pathway (about 10 percent of the total reaction) is assumed to proceed by abstraction of the chlorine atom since a C-Cl bond is weaker than a C-H bond. As for toluene, this pathway leads to benzaldehyde, which reacts further with OH to yield PBzN:

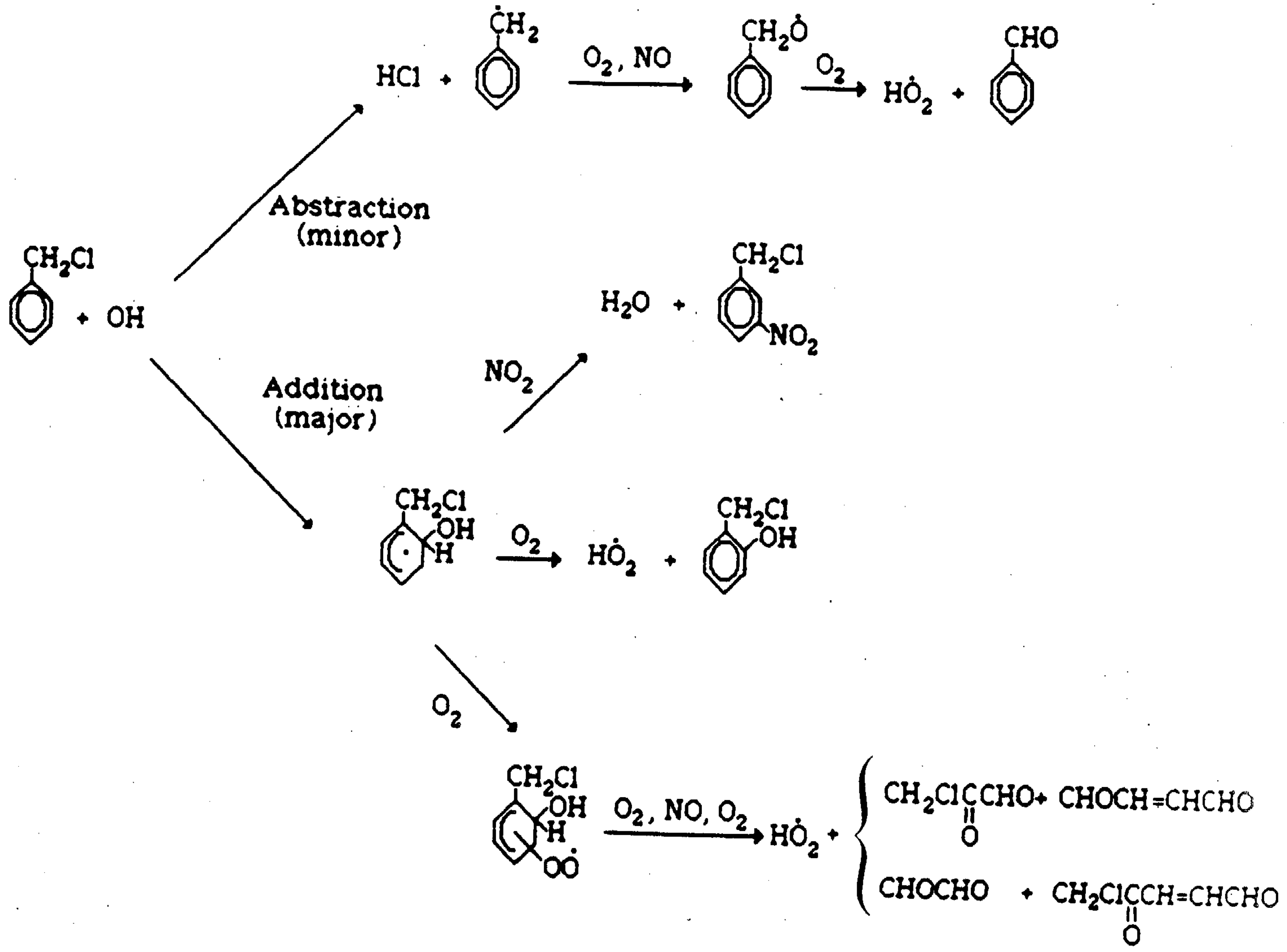
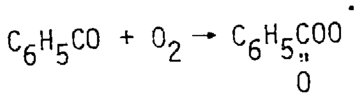
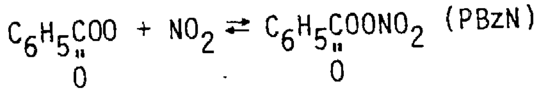


Figure 8.8-1. Reaction of OH with Benzyl Chloride.

$$C_6H_5CHO + OH \rightarrow H_2O + C_6H_5\dot{C}O$$



$$C_6H_5CO + O_2 \rightarrow C_6H_5\underset{\overset{\|}{O}}{C}OO^{\bullet}$$



$$C_6H_5\underset{\overset{\|}{O}}{C}OO + NO_2 \rightleftarrows C_6H_5\underset{\overset{\|}{O}}{C}OONO_2 \text{ (PBzN)}$$

The addition pathway (about 90 percent of the total reaction) involves three competing reactions of the benzyl chloride-OH adduct: reaction with NO_2 to form nitrobenzyl chloride, reaction with oxygen by abstraction to form chloromethyl phenol, and reaction with oxygen by addition to form aliphatic dicarbonyls, chloromethyl glyoxal ($CH_2ClCOCHO$) + 2-butene dial ($CHOCH = CHCHO$) and/or glyoxal ($CHOCHO$) + $CH_2ClCOCH = CHCHO$. These aliphatic carbonyls are in turn rapidly removed by photolysis and by reaction with OH. The relative importance of these three pathways is tentatively estimated to be 5-10 percent (adduct + NO_2), 20-50 percent (adduct + O_2, abstraction) and 40-75 percent (adduct + O_2, addition/ring opening).

8.9 REFERENCES

Farley, C.P. 1985. Personal communication from Environmental Operations, Monsanto Chemical Intermediates, St. Louis, Missouri (10 July).

Felder, J.D. 1985. Personal communication from Product Safety Manager, Monsanto Polymer Products Company, St. Louis, Missouri (6 December).

Gery, M.W., D.L. Fox, H. Jeffries, L. Stockburger and W.S. Weathers. 1985. "A continuous stirred tank reactor investigation of the gas phase reaction of hydroxyl radicals and toluene," International Journal of Chemical Kinetics 17:931-955.

Gledhill, W.E., R.G. Kaley, W.J. Adams, O. Hicks, P.R. Michael, V.W. Saeger and G.A. LeBlanc. 1980. "An environmental safety assessment of butyl benzyl phthalate," Environmental Science and Technology 14(3):301-305.

Grosjean, D. 1985. "Atmospheric reactions of styrenes and peroxybenzoyl nitrate," Science of the Total Environment 46:41-59.

Hill, S. 1985. 1984 toxic use survey: Bay Area Air Quality Management District. Bay Area Air Quality Management District, San Francisco, CA.

ICF (ICF Incorporated). 1985. *Draft Superfund public health evaluation manual*. Prepared for the U.S. Environmental Protection Agency, Office of Emergency and Remedial Response, Office of Solid Waste and Emergency Response, Washington, DC, Appendix C-1

Lane, M. 1986. Personal communication from Emery Industries, Personal Care and Specialties Group, Los Angeles, CA (10 June).

Leone, J.A. and J.H. Seinfeld. 1984. "Updated mechanism for atmospheric photooxidation of toluene," *International Journal of Chemical Kinetics* 16:159-193.

Leone, J.A., R.C. Flagan, D. Grosjean and J.H. Seinfeld. 1985. "An outdoor smog chamber and modeling study of toluene-NO_x photooxidation," *International Journal of Chemical Kinetics* 17:177-216.

Mamola, J. 1985. Personal communication from Stauffer Chemical Company, Los Angeles, CA (15 July).

McCurdy, P.P. 1985. *Chemicalweek buyers' guide '86*. McGraw-Hill, Inc., New York, NY.

Perwak, J., M. Goyer, G. Schimke, A. Eschenroeder, J. Fiksel, K. Scow and D. Wallace. 1981. *An exposure and risk assessment for phthalate esters (di(2-ethylhexyl) phthalate, di-n-butyl phthalate, dimethyl phthalate, diethyl phthalate, di-n-octyl phthalate, butyl benzyl phthalate) (Revised)*. Prepared by A.D. Little, Inc. for the U.S. Environmental Protection Agency, Office of Water Regulations and Standards, Washington, D.C., EPA-440/4-81-020.

SAI (Systems Applications, Inc.). 1980. *Human exposure to atmospheric concentration of selected chemicals: Volume 1*. Prepared for the U.S. Environmental Protection Agency, Research Triangle Park, NC (NTIS: PB81-193252)

Sandberg, M., L. Rittfeldt, and M. Ahlberg. 1984. *Organic air pollutants during manufacturing and handling of PVC floor tiles*. Foersvarets Forskningsanstalt, Umea, Sweden (NTIS: N85-31669).

Smith, T. 1987. Personal communication from Bay Area Air Quality Management District, San Francisco, CA (17 February).

Sommer, ? 1985. Personal communication from UOP, Inc., New York, NY (11 July).

SPI (Society of the Plastics Industry, Inc.). 1980. *1980 Membership directory and buyers guide*. New York, NY.

SRI (Stanford Research Institute). 1981. *Chemical economics handbook*. SRI Information Services, Menlo Park, CA.

9.0
EVALUATION OF CHLOROBENZENE

9.1 PHYSICAL AND CHEMICAL PROPERTIES

Chlorobenzene (also known as monochlorobenzene) is a colorless liquid. Table 9.1-1 summarizes some of its physical and chemical properties.

9.2 DIRECT PRODUCTION

As of 1980, five facilities manufactured chlorobenzene in the United States (Dylewski, 1980). None of them is in California.

9.3 INDIRECT PRODUCTION AND EMISSIONS IN CALIFORNIA

A recent evaluation of data from municipal wastewater treatment plants (Chang et al., 1987) found that wastewater treatment processes in California release about 1.7 tons per year of monochlorobenzene. Over three quarters of these emissions (1.33 tons/year) occur at the South Bayside Wastewater Treatment Facility in Redwood City.

SAIC has identified several forms of indirect production of tri- and tetrachlorobenzenes, which might be applicable to California (see Section 12.3), but no mechanisms for production of monochlorobenzene have been discovered (Johnston et al., 1979).

9.4 INDUSTRIAL USE AND EMISSIONS

Monochlorobenzene is used in a variety of industrial settings. The largest fraction produced goes to process phenol and o- and p-nitrochlorobenzene (approximately 60 percent in 1972; SRI, 1981). The remainder is used to produce the more substituted chlorobenzenes, solvents for the manufacture of adhesives, paints, polishes and waxes, resins, heat-transfer media, dyestuffs, drugs and perfumes (Johnston et al., 1979). Chlorobenzene is not used in phenol production by the PMC Specialties Group in Santa Fe Springs

Table 9.1-1

CHEMICAL DATA SUMMARY FOR CHLOROBENZENE

Property	Value for Chlorobenzene
CAS Registry No.	108-90-7
Synonyms	phenylchloride, monochlorobenzene, chlorobenzol, MCB.
Molecular Weight	112.56
Molecular Formula	C_6H_5Cl
Molecular Structure	
Physical State at STP	Colorless liquid
Boiling Point	132°C
Melting Point	-45°C
Specific Gravity	
Vapor Pressure	8.8 mm Hg at 20°C 11.8 mm Hg at 25°C 15 mm Hg at 30°C
Vapor Density (air=1)	
Solubility	0.5 g/L at 20°C 0.488 g/L at 30°C
Log Partition Coefficient (octanol/H_2O)	2.84[a]
Henry's Law Constant	3.72 atm-L/mole

Source: SAI (1980), unless otherwise noted.

[a] ICF (1985).

(Kaufman, 1986) and Chevron U.S.A. in Richmond closed its phenol production facilities in 1982 (Williams, 1986). Whether chlorobenzene is used in other types of formulations in California is unknown.

Table 9.4-1 lists industrial chlorobenzene emission sources in the San Francisco Bay area, as determined by a Bay Area Air Quality Management District survey (Hill, 1985). Emissions from each user are believed to be less than 0.1 ton/yr.

An herbicide which uses monochlorobenzene as a solvent/carrier is Lasso$^{\text{TM}}$. Lasso is registered for annual grass and broadleaf weed control on corn, soybeans, peanuts, grain sorghum (milo), sunflowers, and woody ornamentals (Jones, 1986). Its primary uses are for corn, soybeans, peanuts, and milo, which are predominantly produced in the midwest. Therefore, considerably less Lasso is used in California than in several midwestern states (Gigax, 1986). Several types of Lasso exist. Alachlor, which is the active ingredient in Lasso, is granular at normal temperatures. Micro tech Lasso and Lasso II contain granular alachlor and no chlorobenzene. Lasso, Lasso Atrazine, and Lasso EC contain different proportions of alachlor and monochlorobenzene.

We contacted Monsanto Agricultural Company regarding the fractions of these Lasso products that chlorobenzene comprises and their California distributions. Monsanto provided data on total monochlorobenzene sales to California (Gigax, 1987). However the ARB has determined that these data are a trade secret and must be kept confidential (Jennings, 1987). California use and emissions from those compounds cannot, therefore, be reported here.

9.5 CONSUMER USE AND EMISSIONS

The potential for consumer exposure to monochlorobenzene appears to be from use of certain herbicides, degreasing agents for automobile parts, and at least one paint formulation.

Table 9.4-1

CHLOROBENZENE EMISSIONS IN THE SAN FRANCISCO BAY AREA

Source	City	Emissions (tons/yr)
Alameda County		
Clorox Technical Center	Pleasanton	U
DOE-Sandia National Laboratory	Livermore	T
Kaiser Aluminum & Chemical Co.	Pleasanton	T
Lawrence Livermore National Laboratory	Livermore	T
Contra Costa County		
Shell Oil Company	Martinez	U
Stauffer Chemical Company	Martinez	0.1
Union Oil Co. of California	Richmond	U
Santa Clara County		
Advanced Micro Devices		U
American Microsystemes, Inc.		T
Ford Aerospace & Communications	Palo Alto	T
National Semiconductor Corp.	Santa Clara	U
Precision Monolithics, Inc.	Santa Clara	U
TRW Microwave Inc.	Sunnyvale	T
United Technologies	San Jose	T
Van Waters & Rogers	San Jose	T
Varian Associates	Palo Alto	T
Verbatim Corporation	Sunnyvale	T
Sonoma County		
Hewlett-Packard Co.	Santa Rosa	T

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

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

The herbicide Lasso, mentioned in Section 9.4, is undoubtedly used to some unknown extent by California consumers. At least one paint formulation, gloss white butyrate lacquer (alkyd modified), contains approximately 22 percent monochlorobenzene by weight as a pigment carrier. The monochlorobenzene is probably released into the air upon application of the paint. Whether these products are used for consumer as well as industrial applications is unknown (Ash and Ash, 1982). Finally, monochlorobenzene is used as a solvent in the manufacture of some types of adhesives. It is also not presently known whether these adhesives are commonly used by consumers.

9.6 EMISSION SUMMARY

Chlorobenzene has been identified in a variety of settings, some of which are known to be present in California. The amount of compound released to the air and the location of the releases are presently unknown. The following summarizes our knowledge about the potential emissions of chlorobenzene in California:

(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. It is likely that some of these industrial applications in California entail the use of chlorobenzene. However, it is not presently known to what extent this is true;

(3) Chlorobenzene is a solvent/carrier in the herbicide Lasso, which is used to control weeds in several food crops as well as woody ornamentals and broadleaf weeds.

(4) Other consumer uses are solvent for gloss white butyrate lacquer, and solvent for certain types of adhesives.

9.7 SUMMARY OF AMBIENT CONCENTRATION DATA

9.7.1 Gas Phase Concentrations

Ambient levels of chlorobenzene have been measured at several locations in California (Table 9.7-1). Concentrations vary widely among investigators. Discrepancies may exist in the data reported by the same investigators in different publications (e.g. Singh et al., 1981; Brodzinsky and Singh, 1983). Concentrations measured outside of California are also listed in Table 9.7-1 for comparison. Discrepancies may exist there too, since urban-suburban concentrations are reported to be substantially higher than those measured at near-source sites. The data set of Guicherit and Schulting (1985), which is internally consistent, indicates chlorobenzene levels of up to 2.5 ppb, with typical mean values of about 0.1 ppb.

9.7.2 Condensed Phase Concentrations

No data are available for chlorobenzene in fog, rain or aerosol samples. With high vapor pressure and low aqueous solubility, chlorobenzene is not expected to accumulate in hydrometeors and aquated aerosols.

9.8 ATMOSPHERIC CHEMISTRY

9.8.1 In-Situ Formation

The reaction of benzene with chlorine atoms, if involving chlorine addition on the aromatic ring followed by adduct reaction with oxygen, may lead to chlorobenzene:

$$\mathrm{C_6H_6 + \dot{C}l \rightarrow (C_6H_6\dot{C}l)}$$

$$\mathrm{(C_6H_6Cl)^{\bullet} + O_2 \rightarrow H\dot{O}_2 + C_6H_5Cl}$$

However, this reaction, if indeed proceeding as is suggested, is expected to be of negligible importance in urban atmospheres. Chlorobenzene formation may take place in industrial atmospheres where both benzene and chlorine may be emitted. Chlorine photolyzes rapidly in sunlight to yield chlorine atoms, and daytime chlorination of benzene to chlorobenzene, toluene to chlorotoluene, etc., may take place under these conditions.

Table 9.7-1

AMBIENT CONCENTRATIONS OF CHLOROBENZENE

(Concentrations in ppb)

	Concentration	
	Mean	Maximum
California		
Los Angeles[a]	~0.2	~0.5
Oakland[a]	~0.1	~0.3
Los Angeles[b]	3.4	21
Oakland[b]	0.64	0.91
Riverside[b]	2.2	8.0
Upland[c]	0.004	0.033
Other Locations		
Phoenix, AZ[a]	~0.2	~0.5
50 urban and near-source sites in the U.S.[b]:		
urban	0.8	21
near source	0.2	5.2
combined	0.66	21
Netherlands (three sites)[d]	0.06-0.1	0.73-2.5
Portland, OR[e]	0.002	0.003

---

[a] Singh et al., 1981. Two weeks of monitoring at each site.

[b] Brodzinsky and Singh, 1983. Probably includes some data already reported by Singh et al., 1981.

[c] Pellizzari, 1979.

[d] Guicherit and Schulting, 1985. Two samples per day per site in 1980.

[e] Ligocki et al., 1985. Seven samples collected during rain events, 1984.

9.8.2 Removal Processes

Photolysis, reaction with ozone, and reaction with the nitrate radical are of negligible importance. Removal of chlorobenzene from the atmosphere will be controlled by its reaction with the hydroxyl radical. The reaction rate constant we estimated from structure-reactivity relationships (see Section 3.2.2.5) is about 2.0 x 10^{-12} cm^3 $molecule^{-1}$ sec^{-1}. The only, and very recent, experimental measurement is that of Davenport et al. (1986), k_{OH} = 9.5 x 10^{-13} cm^3 $molecule^{-1}$ sec^{-1}, i.e. about half our SRR estimate.

Products of the OH-chlorobenzene reaction have not been investigated. A tentative mechanism is given in Figure 9-8.1, with the assumption that the major features of the OH-aromatic hydrocarbon reaction mechanism apply to chlorobenzene as well. There is no H atom abstraction pathway in this case, and OH addition to the aromatic ring is assumed to be in ortho (and para) of the chlorine-bearing carbon atom. As is shown in Figure 9.8-1 for the ortho OH adduct, the adduct may react with NO_2 to form nitrochlorobenzene, with O_2 (abstraction) to yield chlorophenol, and with O_2 (addition) to yield, upon aromatic ring opening, aliphatic dicarbonyl products. These carbonyls include CHOCHO (glyoxal), ClCOCH=CHCHO, CHOCH=CHCHO and ClCOCHO. In turn, the dicarbonyls will be rapidly removed by photolysis and by reaction with OH.

9.9 REFERENCES

Ash, M. and I. Ash. 1982. Formulary of paints and other coatings, Vol. II. Chemical Publishing Co., Inc., New York, NY.

Brodzinsky, R. and H.B. Singh. 1983. Volatile organic chemicals in the atmosphere: an assessment of available data. U.S. Environmental Protection Agency, Research Triangle Park, NC, EPA-600/3-83-027a.

Chang, D.P.Y., E.D. Schroeder, and R.L. Corsi. 1987. Emissions of volatile and potentially toxic organic compounds from sewage treatment plants and collection systems. Prepared by the University of California, Davis, Department of Civil Engineering for the California Air Research Board, Contract No. A5-127-32.

Davenport, J., D.G. Hendry, L. Gu and T. Mill. 1986. "Hydroxyl radical reaction rate constants for organic chemicals in the troposphere: estimation using structure-reactivity relationship and measurements for six chlorinated hydrocarbons." Paper presented at the 192nd Meeting of the American Chemical Society, Division of Environmental Chemistry, Anaheim, CA (8-12 September).

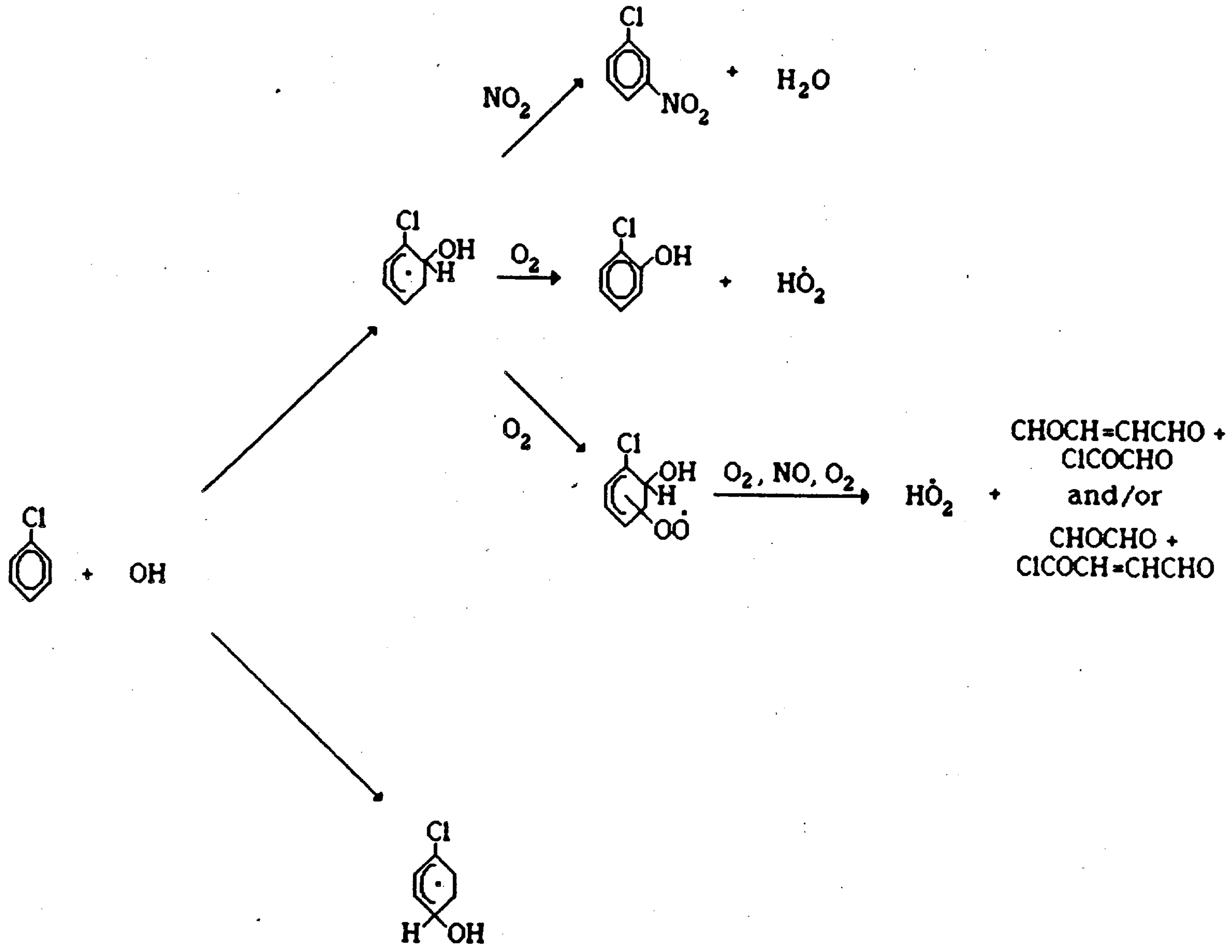


Figure 9.8-1. Reaction of OH with Chlorobenzene.

Dylewski, S.W. 1980. "Chlorobenzenes," Chapter 2 in Organic Chemical Manufacturing. Volume 6: Selected Processes. Prepared by IT Enviroscience for the U.S. Environmental Protection Agency, Emission Standards and Engineering Division, Research Triangle Park, NC, EPA-340/3-80-028a.

Gigax, D. 1986. Personal communication from Technical Supervisor, Commercial Products, Monsanto Agricultural Company, St. Louis, MO (24 July - 11 September).

Gigax, D. 1987. Letter from Technical Supervisor, Commercial Products, Monsanto Agricultural Company, St. Louis, MO, to J. Jennings, California Air Resources Board, Sacramento, CA (8 January).

Guicherit, R. and F.L. Schulting. 1985. "The occurrence of organic chemicals in the atmosphere of the Netherlands," Science of the Total Environment 32:193-219.

Hill, S. 1985. 1984 toxic use survey: Bay Area Air Quality Management District. Bay Area Air Quality Management District, San Francisco, CA.

Jennings, J. 1987. Letter from Staff Counsel, California Air Resources Board, Sacramento, CA, to M. Rogozen, SAIC (26 March).

Johnston, P., P. Bannister, H. Bryson, K. Harer, V. Hodge, J. Meisner, and K. Walker. 1979. Phase I materials balance: Chlorobenzenes. Prepared by Science Applications, Inc. for U.S. Environmental Protection Agency, Office of Toxic Substances, Contract 68-01-5693.

Jones, T. 1986. Letter with label enclosures from Pesticide Registration Branch, California Department of Food and Agriculture (15 July).

Kaufman, C.Y. 1986. Letter from Regulatory Manager, PMC Specialties Group, Inc., Productol Division, Santa Fe Springs, CA to M. B. Rogozen, SAIC (3 February).

Ligocki, M.P., C. Leuenberger and J.F. Pankow. 1985. "Trace organic compounds in rain. II. Gas scavenging of neutral organic compounds," Atmospheric Environment 19:1609-1618.

Pellizzari, E.D. 1979. Information on the characteristics of ambient organic vapors in areas of high chemical production. Prepared for U.S. EPA, Research Triangle Institute, Research Triangle Park, NC.

SAI (Systems Applications, Inc.). 1980. Human exposure to atmospheric concentration of selected chemicals. Volume I. Prepared for the U.S. Environmental Protection Agency, Research Triangle Park, NC (NTIS: PB81-193252).

Singh, H.B., L.J. Salas, A.J. Smith and H. Shigeishi. 1981. "Measurements of some potentially hazardous organic chemicals in urban environments," Atmospheric Environment 15:601-612.

SRI (Stanford Research Institute). 1981. Chemical economics handbook. SRI Chemical Information Services, Menlo Park CA, from Toxicology Data Base on-line service.

SRI (Stanford Research Institute). 1983. Chemical economics handbook. SRI Chemical Information Services, Menlo Park, CA.

Williams, P. 1986. Personal communication from Chevron, U.S.A., Richmond, CA (22 January).

10.0

EVALUATION OF CHLOROPRENE

10.1 PHYSICAL AND CHEMICAL PROPERTIES

Chloroprene is a colorless liquid. Table 10.1-1 summarizes some of its physical and chemical properties.

10.2 DIRECT PRODUCTION IN CALIFORNIA

This chemical is only used captively in the production of neoprene rubber, which is manufactured only by Dupont in LaPlace, Louisiana and Victoria, Texas; and Denka in Houston, Texas. Thus, none of the compound is processed in California (Andrews, 1985; Downes, 1985; SAI, 1980).

10.3 INDIRECT PRODUCTION AND EMISSIONS IN CALIFORNIA

As mentioned in Section 10.8, there are no known atmospheric reactions leading to the formation of chloroprene. To the best of our knowledge, no mechanisms exist for other indirect production of this compound.

10.4 INDUSTRIAL USE AND EMISSIONS

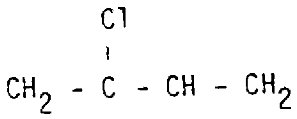
As mentioned in Section 10.2, chloroprene is only used captively in the production of neoprene rubber; no manufacturing facilities are in California.

10.5 CONSUMER USE AND EMISSIONS

Neoprene rubber is used to manufacture oil-resistant rubber goods, automobile parts, wire and cable coatings, gaskets, caulks, and other materials requiring chemical, oil, and weather resistance (USEPA, 1980; SAI, 1980). No data appear to exist on the leakage of chloroprene which may be trapped in finished neoprene products. We may assume that such releases are small, if they exist at all.

Table 10.1-1

CHEMICAL DATA SUMMARY FOR CHLOROPRENE

Property	Value for Chloroprene
CAS Registry No.	126-99-8
Synonyms	2-chlorobutadiene-1,3, 8-chloroprene, chloroprene, 2-chloro-1, 3-butadiene
Molecular Weight	88.54
Molecular Formula	C_4H_5Cl
Molecular Structure	 $CH_2 - \overset{Cl}{\overset{\vert}{C}} - CH - CH_2$
Physical State at STP	Liquid-colorless, flammable
Boiling Point	59.4°C at 760 mm
Melting Point	-130°C
Specific Gravity	0.9583 at 20°C/4°C
Vapor Pressure	215.4 mm at 25°C
Vapor Density (air=1)	3.06
Solubility	Slightly soluble (<10.0 g/L of H_2O)
Log Partition Coefficient (octanol/H_2O)	
Henry's Law Constant	

Source: SAI (1980); Verschueren (1977).

10.6 EMISSION SUMMARY

No emissions of chloroprene to the California air are presently known. All production of this compound is used captively in the manufacture of neoprene rubber.

10.7 SUMMARY OF AMBIENT CONCENTRATION DATA

There are no published data on ambient levels of chloroprene, in California or elsewhere.

10.8 ATMOSPHERIC CHEMISTRY

10.8.1 In-Situ Formation

There are no known reactions that would lead to in-situ formation of chloroprene, $CH_2=C(Cl)CH = CH_2$, in the atmosphere. The reaction of chlorine with butadiene, of possible importance near sources of these two compounds, would lead to products other than chloroprene.

10.8.2 Removal Processes

No kinetic data are available for the reactions of chloroprene with OH, O_3, and NO_3. However, our estimates from structure-reactivity relationships:

$$k_{OH} = 6.2 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$$

$$k_{O_3} = 1.4 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$$

$$k_{NH_3} = 3.6 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$$

indicate rapid removal of chloroprene by all three reactions. No experimental studies of reaction products have been carried out. Tentative mechanisms are outlined in Figure 10.8-1 for the chloroprene-ozone reaction and in Figure 10.8-2 for the chloroprene-OH reaction.

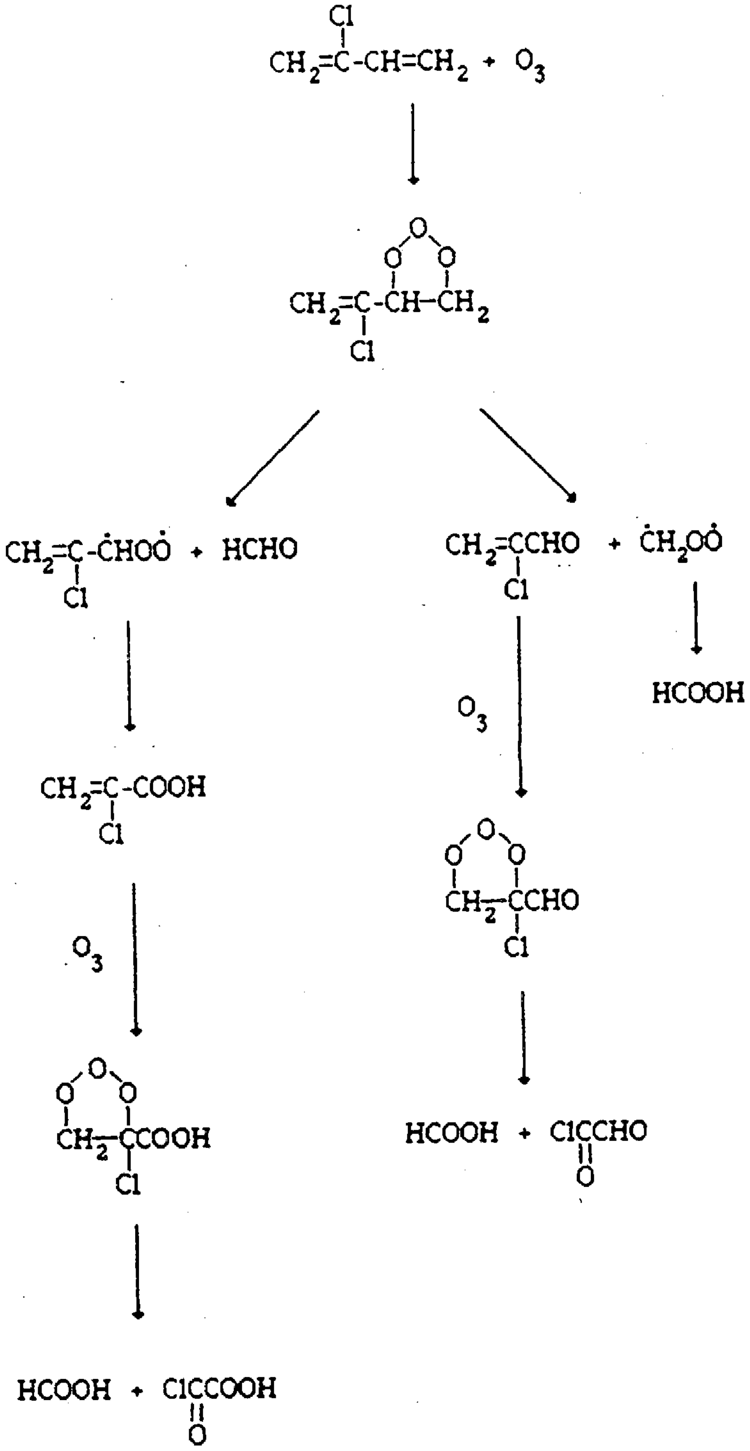


Figure 10.8-1. Ozone-Chloroprene Reaction.

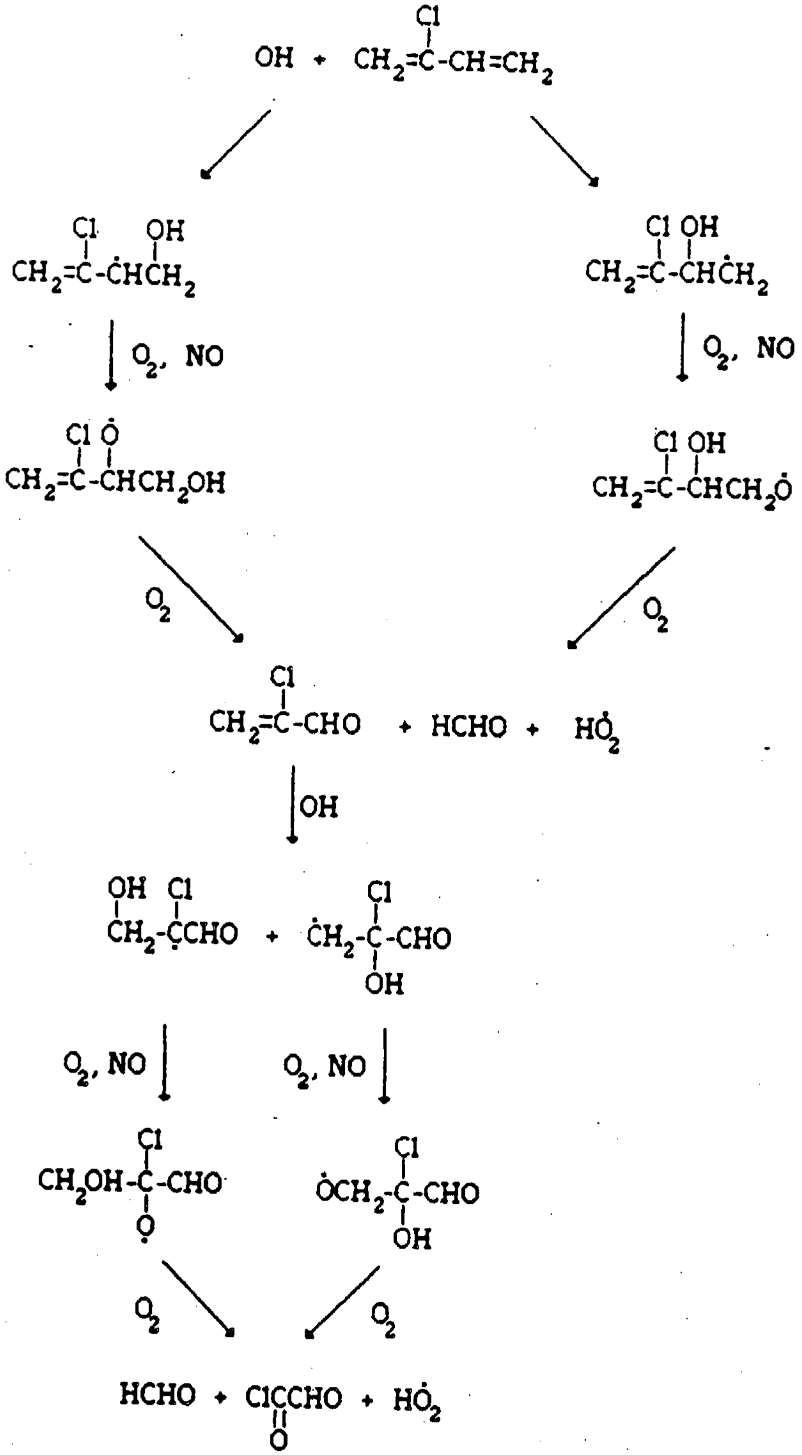
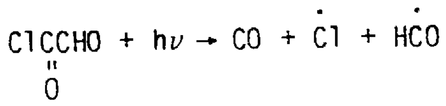


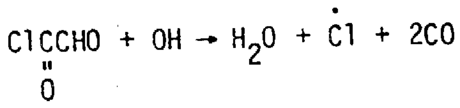
Figure 10.8-2. OH-Chloroprene Reaction.

Addition of ozone (Figure 10.8-1) is expected to take place preferentially on the C_3-C_4 double bond since the chlorine atom substituent on the C_2 carbon decreases the electronic density of the C_1-C_2 bond. Unimolecular decomposition of the ozonide and rearrangement of the resulting Criegee biradicals lead to $CH_2=C(Cl)CHO$ and $CH_2=C(Cl)COOH$. These compounds may in turn react with ozone to yield the acyl chlorides ClCOCHO and ClCOCOOH, respectively.

Addition of OH (Figure 10.8-2) is also assumed to involve preferentially the C_3-C_4 bond, followed by the "normal" alkyl $\xrightarrow{O_2}$ peroxy $\xrightarrow{NO}$ alkoxy $\rightarrow$ unimolecular decomposition reaction sequence. The first generation product, $CH_2=C(Cl)CHO$, may react with OH (or with ozone as shown in Figure 10.8-1) to yield ClCOCHO. In turn, ClCOCHO and ClCOCOOH are expected to be rapidly removed from the atmosphere by photolysis and by reaction with OH, e.g.:



$$\mathrm{Cl}\underset{\underset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{CHO} + h\nu \rightarrow \mathrm{CO} + \dot{\mathrm{C}}\mathrm{l} + \mathrm{H\dot{C}O}$$



$$\mathrm{Cl}\underset{\underset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{CHO} + \mathrm{OH} \rightarrow \mathrm{H_2O} + \dot{\mathrm{C}}\mathrm{l} + 2\mathrm{CO}$$

10.9 REFERENCES

Andrews, V. 1985. Personal communication from Denka Chemical Company, Houston, TX (16 July).

Downes, M. 1985. Personal communication from E.I. DuPont de Nemours & Co., Wilmington, DE (11 July).

SAI (Systems Applications, Inc.). 1980. Human exposure to atmospheric concentration of selected chemicals: volume 2. Prepared for the U.S. Environmental Protection Agency, Research Triangle Park, NC (NTIS: PB81-193252).

USEPA (U.S. Environmental Protection Agency). 1980. Organic chemical manufacturing volume 10: selected processes. Office of Air Quality Planning and Standards, Research Triangle Park, NC, EPA-450/3-80-028e.

Verschueren, K. 1977. Handbook of environmental data on organic chemicals. Van Nostrand Reinhold Company, New York, NY.

11.0
EVALUATION OF CRESOLS

11.1 PHYSICAL AND CHEMICAL PROPERTIES

Cresols are produced as by-products of either coal tar distillation or petroleum naphtha cracking. In these by-product mixtures, cresols are defined as the compounds, usually comprising phenols, cresols, and xylenols (Kaufman, 1986a), with boiling points below 204°C, while cresylic acids are those compounds with boiling points above 204°C (SAI, 1980). Three cresol isomers exist: ortho-cresol, meta-cresol, and para-cresol. Byproduct mixtures generally contain about 31 percent ortho-, 43 percent meta- and 26 percent para-cresol.

Ortho-cresol has a solid crystalline structure at room temperature, and has a phenolic odor. Para-cresol is also a solid crystal with a phenolic odor. Meta-cresol is a colorless or yellowish liquid with a phenolic odor. Tables 11.1-1 through 11.1-3 summarize some of the physical and chemical properties of the three isomers.

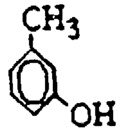
11.2 DIRECT PRODUCTION IN CALIFORNIA

Six companies manufactured mixed cresols in 1980, with total domestic production of approximately 32 million pounds. Eight companies produced cresylic acids during that same period. The only California manufacturer of either cresols or cresylic acid was Ferro Corporation in Santa Fe Springs (SAI, 1980). Ferro Corporation has recently changed management and is now called the PMC Specialties Group, Inc.; the company still manufactures these compounds at Santa Fe Springs.

In 1978, the Ferro Corporation was estimated to have produced approximately 4 million lb of mixed cresols, 3 million lb of o-cresol, and 5 million lb of cresylic acid (SAI, 1980). Using an emission factor of 0.0025 lb of cresol or cresylic acid per pound of product (SAI, 1980), the estimated 1978 emissions of mixed cresols was 10,000 lb (5 tons), while the figure for the o-cresol

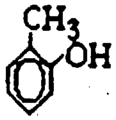
Table 11.1-1

CHEMICAL DATA SUMMARY FOR M-CRESOL

Property	Value for m-cresol
CAS Registry No.	108-39-4
Synonyms	m-cresylic acid, 3-methylphenol, m-hydroxytoluene
Molecular Weight	108.13
Molecular Formula	C_7H_8O
Molecular Structure	
Physical State at STP	Liquid - colorless or yellowish
r Boiling Point	202.8°C
?rMelting Point	12°C
?r Specific Gravity	1.0341 at 20°C/4°C
Vapor Pressure	0.075 mm at 20°C
Vapor Density (air=1)	3.72
Solubility	Slightly soluble (23.5 g/L of H_2O) at 20°C
Log Partition Coefficient (octanol/H_2O)	2.37
Henry's Law Constant	

Source: SAI (1980), Verschueren (1977), Weber et al. (1981).

Table 11.1-2
CHEMICAL DATA SUMMARY FOR O-CRESOL

Property	Value for o-cresol
CAS Registry No.	95-48-7
Synonyms	o-cresylic acid, o-hydroxytoluene, 2-methylphenol
Molecular Weight	108.13
Molecular Formula	C_7H_8O
Molecular Structure	
Physical State at STP	Solid crystals - non-volatile
Boiling Point	190.8°C
Melting Point	30.9°C
Specific Gravity	1.047 at 20°C/4°C
Vapor Pressure	0.3 mm at 20°C
Vapor Density (air=1)	3.72
Solubility	Soluble (31 g/L of H_2O at 40°C)
Log Partition Coefficient (octanol/H_2O)	3.40
Henry's Law Constant	

Source: SAI (1980), Verschueren (1977), Weber et al. (1981).

Table 11.1-3

CHEMICAL DATA SUMMARY FOR P-CRESOL

Property	Value for Cresol
CAS Registry No.	106-44-5
Synonyms	4-cresol, 4-methylphenol, p-hydroxytoluene, p-cresylic acid
Molecular Weight	108.13
Molecular Formula	C_7H_8O
Molecular Structure	
Physical State at STP	Solid crystals
Boiling Point	201.8°C
Melting Point	35.26°C
Specific Gravity	1.0341 at 20°C/4°C
Vapor Pressure	0.075 mm at 20°C
Vapor Density (air=1)	3.72
Solubility	Slightly soluble (24.0 g/L of H_2O at 40°C)
Log Partition Coefficient (octanol/H_2O)	2.35
Henry's Law Constant	

Source: SAI (1980), Verschueren (1977), Weber et al. (1981).

isomer was 16,500 lb (8.3 tons); for cresylic acid, emissions were 7,500 lb (3.8 tons). Total emissions in 1978 were, therefore, 34,000 lb (17 tons).

PMC Specialties supplied SAIC with 1984 and 1985 production figures, from which emissions were estimated (Kaufman, 1986b). We may not release these results, since the information is considered proprietary and PMC Specialties is the sole manufacturer of cresols and cresylic acid in the State. Production and emission data have been reported separately to the ARB.

11.3 INDIRECT PRODUCTION AND EMISSIONS IN CALIFORNIA

The major anthropogenic source for indirect emissions of cresols is coke ovens, since coal tars contain 1.04 percent cresols. Until recently, Kaiser Steel Corporation, in Fontana, operated the only coke oven in California. The termination of coking operations left no indirect production source in the state. However, as discussed in Section 11.8, cresols may be formed from toluene in the presence of OH in the atmosphere. Since toluene is an abundant hydrocarbon in the urban environment, and cresol yields from toluene range from 13 to 60 percent, ample opportunity exists for in-situ formation of cresols. (See Section 11.8-1.)

11.4 INDUSTRIAL USE AND EMISSIONS

Industrial uses for mixed cresols and cresylic acids in 1978 included manufacture of tri-cresylic phosphate (TCP) and cresyl diphenol phosphate (CDP) (32 percent), production of phenolic resins (21 percent), use as a wire enamel solvent (21 percent), manufacture of pesticides (8 percent), ingredient in disinfectants/cleaning compounds (3 percent), ore flotation (3 percent), and miscellaneous other minor uses (7 percent).

O-cresol is used to manufacture 2,6-di-tert-butyl-p-cresol (BHT), a food preservative and anti-oxidant. This use consumed approximately half of o-cresol isomer production, while the production of other anti-oxidants consumed another 33 percent, exports accounting for the final 17 percent of production. Approximately half of all p-cresol is exported, one third is used in the manufacture of phenolic resins, and the remaining third in the production of pesticides. Meta-cresol is used exclusively in the manufacture of pyrethroid pesticides.

Of the three primary manufacturing uses for cresols, BHT production, pyrethroid pesticides, and tri-cresyl phosphate, only BHT manufacture was known to have taken place in California. Shell Chemical Company, at its facility in Martinez, manufactured food grade BHT, using approximately 10 million lb of o-cresol in 1978. However, Shell Chemical stopped production of BHT approximately 6 to 8 years ago, in part due to foreign competition (Tonti, 1986). It appears that no manufacturers of BHT remain in California.

It is not presently known to what extent the other itemized industrial uses for cresols take place within the state. However, using 1980 emissions data for these various end uses, reported by region, we made a preliminary first-cut approximation of California emissions from cresol use. End-use production data for cresol users in California for phenolic resins, pesticides, wire enamel solvent, or mining activity using ore flotation agents are unavailable. In order to estimate the quantity of cresol emissions in the state from these activities, we used a 1980 emissions estimate for each activity for the Pacific region (SAI, 1980). These data were then apportioned to California on the basis of population. California's proportion of the Pacific region population in 1983 was 0.734 (USDOC, 1985). It must be kept in mind that these results are a rough approximation to California emissions since (1) we have not confirmed the actual production, or amount of use, of cresols in California, and (2) the exact proportion of each of these industrial activities within the state may differ from 0.734 in varying degrees. Table 11.4-1 reports the number of production sites in the Pacific region and the estimated emissions for each end-use. As indicated, total emissions in 1978, due to cresol end-use industrial activities, was 1,427,500 lb (714 tons).

In a survey of toxic compound use in the San Francisco Bay area, the Bay Area Air Pollution Control District identified three facilities from which cresol emissions may exceed 0.1 tons per year (Hill, 1985). Two of these

Table 11.4-1

ESTIMATE OF COMBINED CRESOL EMISSIONS IN CALIFORNIA (1978)

Activity	Pacific Region Emissions[a] (lb/yr)	California Emissions (lb/yr)
Phenolic Resins	24	15,502
Pesticides	13	446
Wire Enamel Solvent	174	1,340,368
Ore Flotation Agent	22	71,164
Total		1,427,481

[a] Estimated by SAI, 1980; California emissions based on apportionment by population.

facilities manufacture floppy disks. Facilities where cresol isomers were reported to be used are shown in Table 11.4-2. Total estimated emissions for the Bay Area were 5.2 tons per year, which is far below the rough estimate presented above. There is thus considerable uncertainty in our estimate of total statewide cresol emissions.

11.5 CONSUMER USE AND EMISSIONS

Consumer products in which cresols or cresylic acids are generally found include metal degreasing agents, inks, disinfectants and cleaning compounds. Three percent of mixed cresol production was used in the manufacture of disinfectants and cleaning compounds.

A literature search revealed some product-related information on cresols. Formulations of external carburetor and engine cleaners contain up to 25 percent by weight cresols or cresylic acids. Cresols may also be contained in large percentages (over 50 percent) in some paint removers. Cresols may be contained in permanent, opaquing, and stamping inks. Concentrations of cresols in these products are generally quite low (Gosselin et al., 1984).

We estimated California emissions from disinfectant/cleaning compounds and other miscellaneous uses by apportioning the U.S. emission estimates (SAI, 1980) to California, using a multiplier of 0.11 (USDOC, 1985).

Thus, emissions from disinfectants/cleaning compounds are 273,000 lb (137 tons), while those from miscellaneous other consumer uses are 638 lb (0.3 ton). Total emissions are estimated to be 137 tons.

11.6 EMISSION SUMMARY

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. The likely California industrial end-uses for cresols and cresylic acids are manufacture of TCP and CDP, production of phenolic resins, use as a solvent for wire hanger enamel, manufacture of pesticides, and use as an ore

Table 11.4-2

CRESOL EMISSIONS IN THE SAN FRANCISCO BAY AREA

Source	City	Emissions (tons/yr)
Alameda County		
Alameda Naval Air Station	Alameda	U
DOE-Sandia National Laboratory	Livermore	4.3
Kaiser Aluminum and Chemicals	Pleasanton	T
Lawrence Livermore National Laboratory	Livermore	T
Peterbilt Motors Company	Newark	T
Sherwin-Williams Company	Emeryville	T
World Airways, Inc.	Oakland	U
Contra Costa County		
Chevron Research Company	Richmond	T
Great Western Chemical Co.	Richmond	T
IT Corporation	Martinez	U
Shell Oil Company	Martinez	U
U.S. Steel Corporation	Pittsburg	T
Santa Clara County		
Beckman Instruments, Inc.	Palo Alto	T
Burke Industries, Inc.	San Jose	U
Dysan Corporation	Santa Clara	0.3
Hewlett-Packard Co.	SAnta Clara	T
National Semiconductor Co.	Santa Clara	U
Varian Associates	Palo Alto	T
Velcon Filters, Inc.	San Jose	T
Xidex Corporation	Sunnyvale	0.6
Solano County		
Mare Island Naval Shipyard	Vallejo	U
Travis Air Force Base	Travis AFB	T

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

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

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 consumer products which contain cresols; minor uses for cresols 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 868 tons/yr (787 MT/yr).

11.7 SUMMARY OF AMBIENT CONCENTRATION DATA

11.7.1 Gas Phase Concentrations

Ambient concentrations of cresols have seldom been measured (Table 11.7-1). Data for California consist of a single report (Pellizzari, 1979) for o-cresol in Upland. Fourteen samples were collected near a phenolic resin plant. The mean and maximum o-cresol concentrations were 6.0 and 29 ppb respectively. Data for other near-source samples are included in Table 11.7-1 for comparison. There are no data for near-source concentrations of m-cresol and p-cresol. Data for urban levels of cresols are equally scarce. No data are available for California, and only one recent study (Leuenberger et al., 1985) reports on ambient levels of o-cresol (up to 30 ppt) and m+p cresol (unresolved, up to 50 ppt) in Portland, OR.

11.7.2 Condensed Phase Concentrations

Cresols have high vapor pressures (0.08 - 0.3 mm Hg at 20°C) and are readily soluble in water (18 - 26 g/L at 25°C). As a result, hydrometeor scavenging of gas phase cresols is expected to be important in the atmosphere. Rainwater concentrations of cresols have been reported in only one study (Leuenberger et al., 1985), and the results are listed in Table 11.7-1 along with the corresponding gas phase concentrations. No data are available for rainwater samples collected in California, or for cresols in fog and cloudwater.

Table 11.7-1

AMBIENT CONCENTRATIONS OF CRESOLS

Isomer(s)	Sample Type	Location	Number of Samples	Gas Phase (ppb) Mean	Gas Phase (ppb) Max	Rainwater (g/L)	Reference
Ortho-cresol	Near source:	Upland, CA	14	6.0	29	-	Pellizzari, 1979
		Baton Rouge, LA	2	0.1	0.1	-	Pellizzari, 1979
		El Paso, TX	22	3.8	8.8	-	Pellizzari, 1979
		Houston, TX	8	0.3	0.4	-	Pellizzari, 1979
		S. Charleston, WV	8	0.3	0.5	-	Pellizzari, 1979
		Nagoya, Japan	1	40	-	-	Hoshika and Muto, 1978
	Ambient:	Portland, OR	7	0.016	0.03	0.24-2.8	Leuenberger et al., 1985
Meta-cresol	No Data						
Para-cresol	No Data						
m + p cresol	Near-source:	-	-	-	-	-	-
	Ambient:	Portland, OR	7	0.03	0.05	0.38-2.0	Leuenberger et al., 1985

11.8 ATMOSPHERIC CHEMISTRY

11.8.1 In Situ Formation

The reaction of aromatic hydrocarbons with OH leads to the formation of phenols in the atmosphere: phenol from benzene, cresols from toluene, dimethyl phenols from the xylenes, and so on.

The OH-toluene reaction mechanism is summarized in Figure 11.8-1. The three major pathways are that of OH abstraction, OH addition followed by adduct reaction with O_2 by addition, and OH addition followed by adduct reaction with O_2 by abstraction. The latter pathway yields cresols + HO_2.

The relative importance of these three pathways has been the object of extensive investigations, but major uncertainties still exist. A summary of product yields measured to date is given in Table 11.8-1. Cresols are seen to account for 13 to 60 percent of the total OH-toluene reaction.

Because of the ortho-para orientation effect of the CH_3 group, addition of OH to the toluene aromatic ring takes place preferentially at the C_2 (ortho) and C_4 (para) carbon atoms (Figure 11.8-2). The expected relative abundance of the three cresol isomers is thus ortho $\geq$ para >> meta. While ortho-cresol has indeed been identified as a major reaction product of toluene by several investigators, little data exists concerning the yields of para-cresol and meta-cresol. The available information concerning isomer distribution is summarized in Table 11.8-2. As expected, ortho-cresol accounts for about 80 percent of the total cresols.

The precursor of cresols in polluted air, toluene, is one of the most abundant hydrocarbons in urban atmospheres. This reflects, to some extent, the high aromatic content of unleaded fuels. According to the 1974 Air Resources Board inventory, 77 x 10^3 kg/day of toluene are emitted in the South Coast Air Basin. The most recent comprehensive study of ambient measurements of hydrocarbons in the Los Angeles area (Grosjean and Fung, 1984) reports 6 - 9 a.m. toluene concentrations of 20 - 68 ppb at a downtown Los Angeles

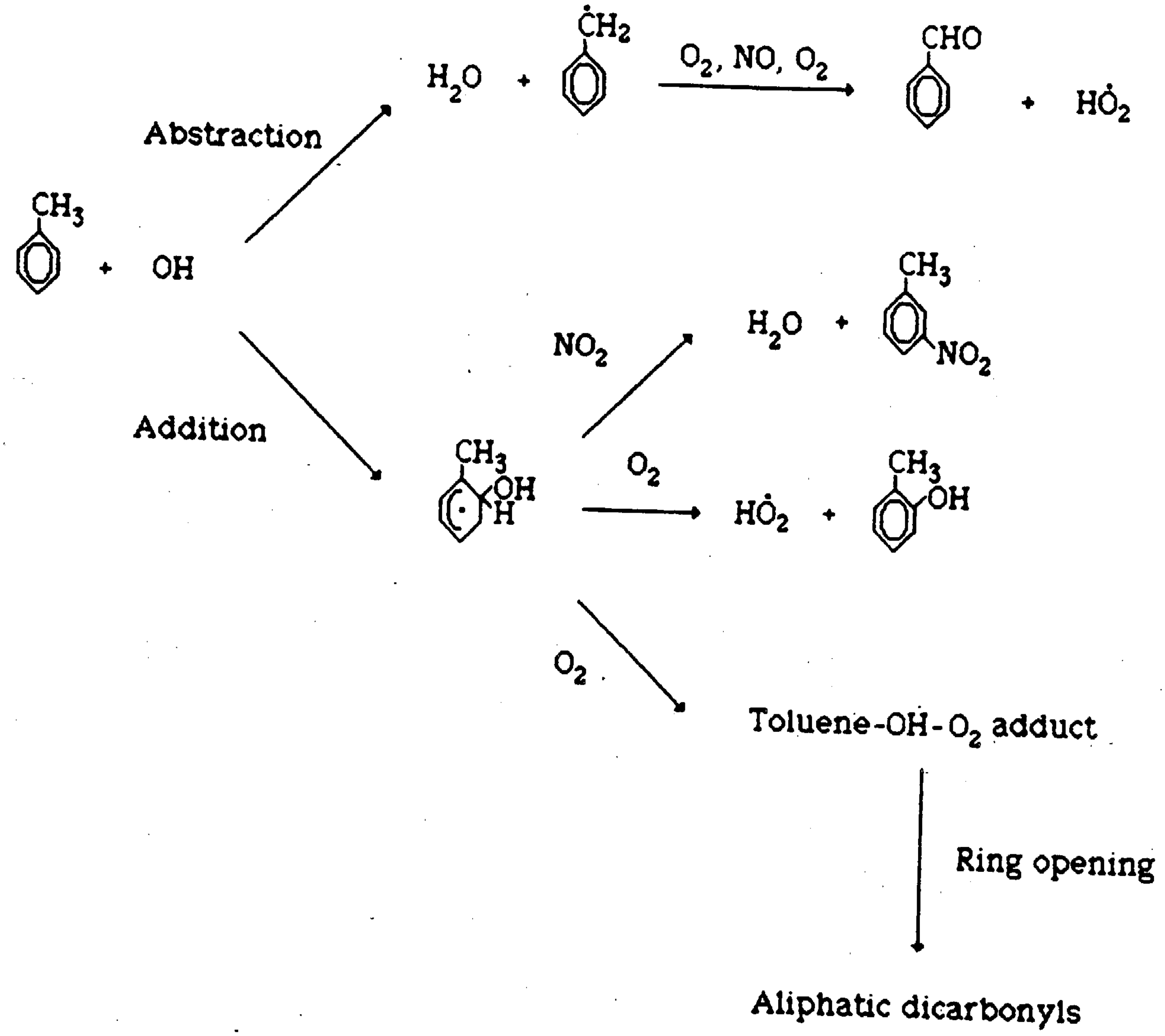


Figure 11.8-1. OH-Toluene Reaction.

Table 11.8-1

PRODUCTS YIELDS[a] FROM TOLUENE
(OH-INITIATED NO_x-AIR PHOTOOXIDATION)

Reference	OH abstraction[b]	OH addition, O_2 addition[c]	OH addition, O_2 abstraction[d]
Akimoto et al., 1978	+[e]		+[f]
Hoshino et al., 1978	+		+[f]
Atkinson et al., 1980	8-22	17-75[g]	16
Kenley et al., 1981	15 ± 2		36-42
Besemer, 1982	3-7	28-39	1-2
Atkinson et al., 1983	7±2	-	13±7
Tuazon et al., 1984	-	25±2[h]	-
Shepson et al., 1984	5	20	+
Dumdei and O'Brien, 1984	+	+	+
Leone et al., 1985	8	$\geq$ 5[i]	20
Gery et al., 1985	13±4	-	45-60 (estimated)
Bandow et al., 1985	11±1	29	60 (estimated)

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[a] Yields in molecules of product formed per molecule of toluene reacted.

[b] Benzaldehyde, benzyl nitrate.

[c] Ring opening products: aldehydes, dicarbonyls, PAN.

[d] Cresols, nitrocresols.

[e] Identified but yield not measured.

[f] Cresols yield about twice the benzaldehyde yield.

[g] From formaldehyde and PAN.

[h] Glyoxal + methyl glyoxal.

[i] From PAN.

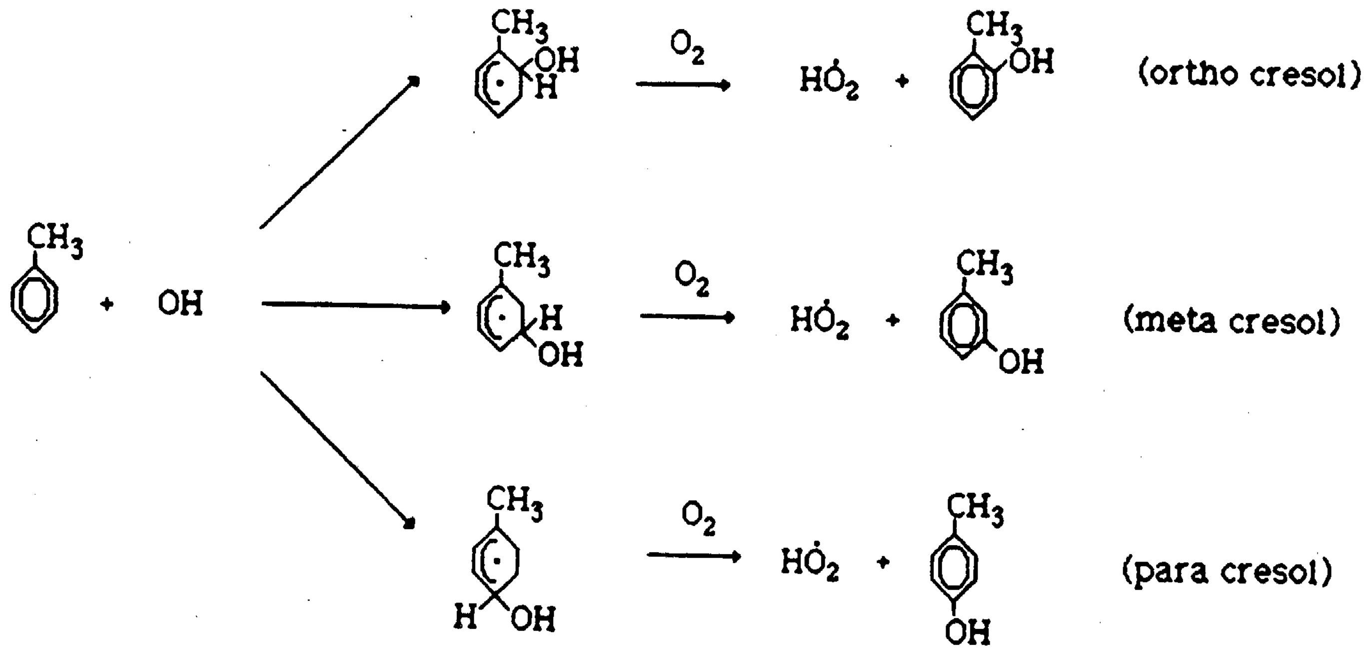


Figure 11.8-2. Cresol Isomer Distribution from the Toluene-OH Addition Pathway.

Table 11.8-2

CRESOL ISOMER DISTRIBUTION FROM TOLUENE

Reference	Percent of Total Cresol Yield ortho cresol	 meta cresol	 para cresol
Akimoto et al., 1978	≥ 80	(m+p) unresolved, ≤ 20	
Hoshino et al., 1978	≥ 80	(m+p) unresolved, ≤ 20	
Atkinson et al., 1980	+[a]	ND	ND
Kenley et al., 1981	80	5	14
Besemer, 1982	+	ND	+
Atkinson et al., 1983	+	ND	ND
Shepson et al., 1984	+	ND	ND
Dumdei and O'Brien, 1984	+, isomer(s) not specified		
Leone et al., 1985	+	ND	ND
Gery et al., 1985	80	5	15

[a] Identified, isomer yields not reported.

[b] ND = No data

location (University of Southern California campus). With reported cresol yields of 13 to 60 percent of the reacted toluene, 10 - 46 x 10^3 kg/day of cresols may be produced in-situ during smog episodes. In the absence of removal processes, ambient levels of cresols in Los Angeles would be as high as 40 ppb. However, cresols react with OH faster than toluene does, and furthermore, also react with the NO_3 radical at night. These rapid removal processes are described in the next section.

11.8.2 Removal Processes

Kinetic information is available for the reaction of cresols with OH, O_3 and NO_3. Photolysis of cresols is negligible. Reaction rate constants are as follows (units: cm^3 $molecule^{-1}$ sec^{-1}):

	ortho-cresol	meta-cresol	para-cresol
$\dot{O}H$	4.7×10^{-11}	6.7×10^{-11}	5.2×10^{-11}
O_3	2.5×10^{-19}	1.9×10^{-19}	4.7×10^{-19}
$NO_3^{\bullet}$	1.2×10^{-11}	0.92×10^{-11}	1.3×10^{-11}

During the daytime, cresols will be rapidly removed from the atmosphere by their reaction with OH and, to a lesser extent, with NO_3. Removal by reaction with ozone will be of minor importance (up to 5 percent of total cresol removal for $O_3 \geq 0.1$ ppm). Reaction with the nitrate radical will result in rapid removal of cresols and in the formation of nitric acid at night. Reaction mechanisms are summarized below for each cresol isomer. Detailed experimental data are available for ortho-cresol, which is the major isomer (about 80 percent of total cresols) formed in the atmospheric oxidation of toluene. Limited or no information is available for meta-cresol and para-cresol. For these two isomers, reaction mechanisms are based on that for ortho-cresol.

The OH-initiated photooxidation of o-cresol (Grosjean, 1984) is similar to that of toluene discussed in the preceding section. Major features of the o-cresol-OH reaction are summarized in Figure 11.8-3. OH reacts with o-cresol by two pathways, one involving H-atom abstraction and the other

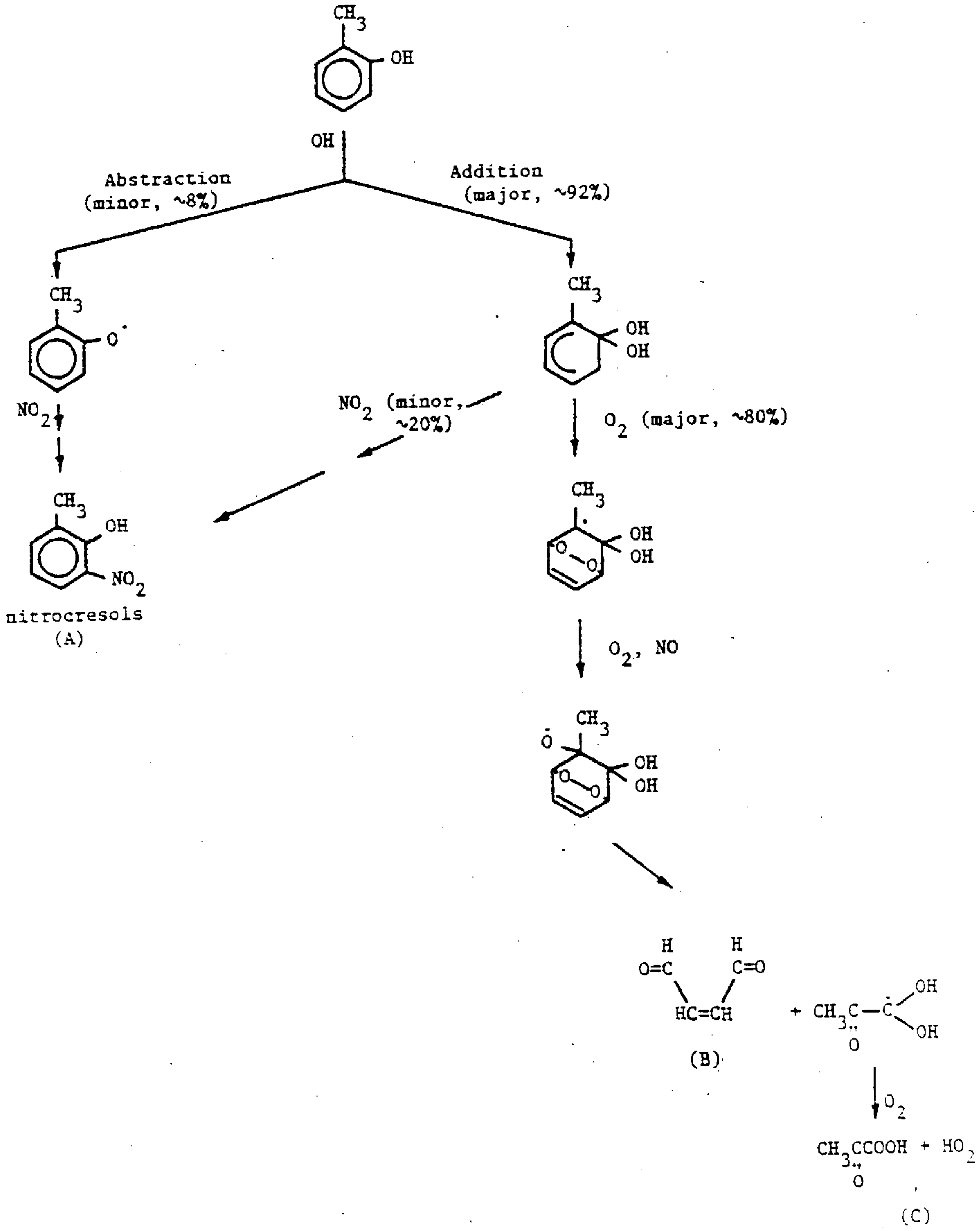
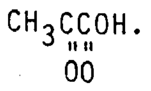


Figure 11.8-3. Tentative Photooxidation Mechanism for Ortho Cresol. Further Reactions of Nitrocresols (A), Cis-2-butene-1,4-dial (B) and Pyruvic Acid (C) not shown. From Grosjean (1984).

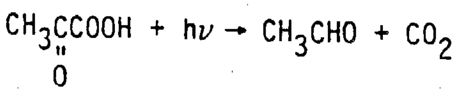
involving addition to the aromatic ring. Addition is the major pathway (about 92 percent of total OH reaction), with OH adding preferentially on the OH-bearing carbon atom. Abstraction (minor, about 8 percent of the total reaction) involves only one hydrogen atom, that of the weak phenolic group. The methyl phenoxy radical thus formed reacts with NO_2 to form nitrocresols. Nitrocresols are also formed by reaction of the cresol-OH adduct with NO_2 (Figure 11.8-4). Nitrocresols are thus formed in high yields, about 26 percent of the total OH-cresol reaction. The cresol-OH adduct also reacts with O_2, resulting in aromatic ring opening and in the formation of aliphatic carbonyl products including ketoacids such as pyruvic acid,



$CH_3\underset{O}{\underset{\|}{C}}\underset{O}{\underset{\|}{C}}OH$.

As for aromatic hydrocarbons, there is still considerable uncertainty regarding the relative importance of "ring conserving" and "ring opening" pathways.

Further reactions of the "first generation" products have been studied experimentally. Pyruvic acid, a ring opening product, reacts only slowly with OH but photolyzes rapidly in sunlight (Grosjean, 1983) to form acetaldehyde:



$$CH_3\underset{O}{\underset{\|}{C}}COOH + h\nu \rightarrow CH_3CHO + CO_2$$

which, in turn, yields peroxyacetyl nitrate (PAN), formaldehyde (a Level 1 compound), and free radicals. Nitrocresols react with OH and with NO_3 to form dinitrocresols (Figure 11.8-5), hydroxynitrocresols (Figure 11.8-6), and, as yet, poorly characterized ring opening products (Grosjean, 1985). The dinitrocresols and other polysubstituted phenols have low vapor pressures and may condense as aerosols. Indeed, aerosol formation from cresols is substantial, accounting for 5 - 19 percent of the reacted o-cresol (Grosjean, 1984) and for up to 57 percent of the reacted nitrocresol (Grosjean, 1985) in experiments involving sunlight irradiation of o-cresol-NO_x mixtures in air.

Atmospheric reactions of m-cresol and p-cresol have not been studied in detail, but reaction mechanisms can be proposed that are essentially identical to that for o-cresol, i.e. that predict the formation of nitrocresols, aliphatic carbonyls and ketoacids, and their respective reaction products.

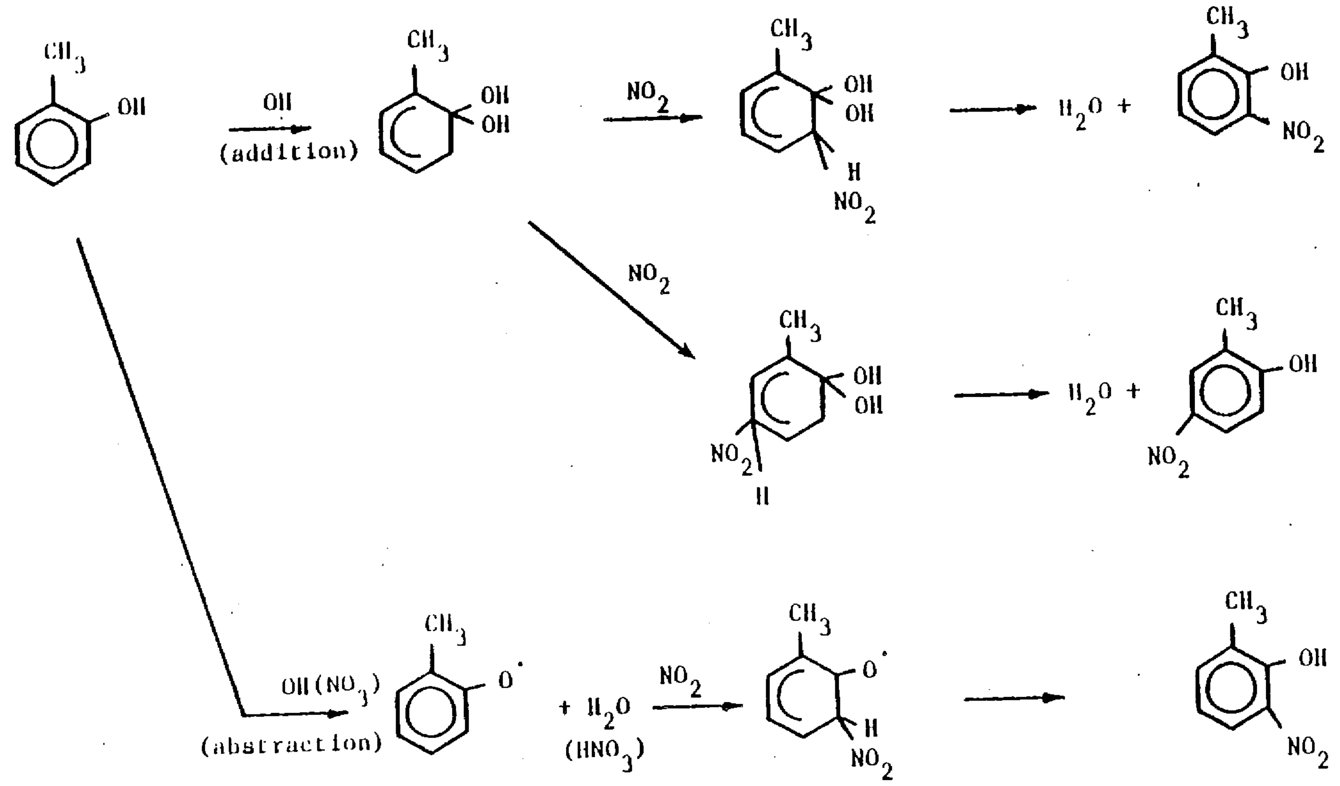


Figure 11.8-4. Nitrocresol Formation Pathways. Top: Reaction of NO_2 with OH-o-cresol adduct. Bottom: Reaction of NO_2 with Phenoxyradical.

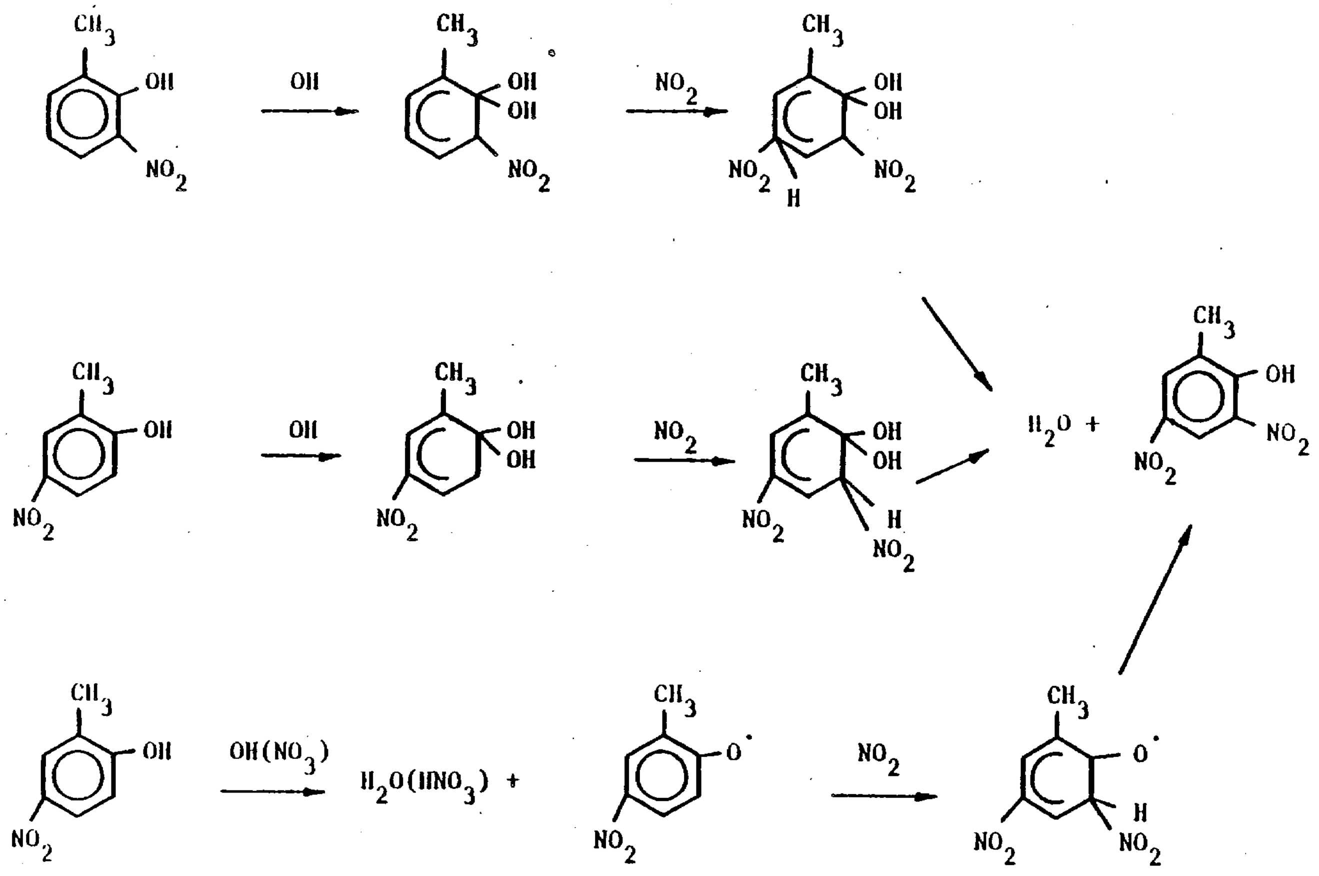


Figure 11.8-5. Dinitrocresol Formation from OH Addition on 2-hydroxy-3-nitrotoluene (top) and 2-hydroxy-5-nitrotoluene (middle) and from OH (or NO_3) Abstraction (bottom, shown for only one nitrocresol isomer).

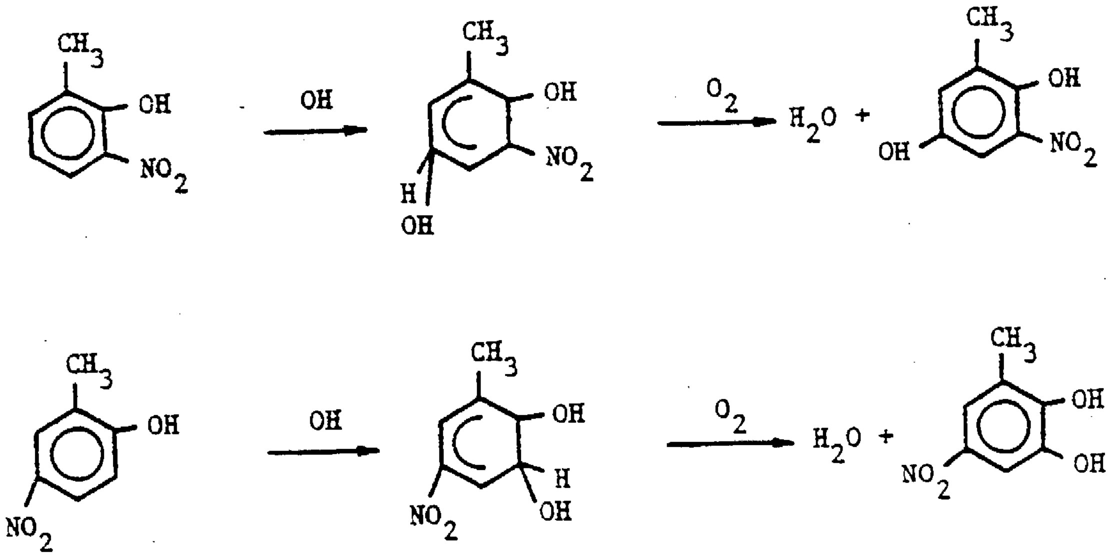


Figure 11.8-6. Tentative Mechanism Consistent with Hydroxynitrocresol Formation from Nitrocresols (Adduct Reaction with NO_2 and Aromatic Ring Opening Omitted for Clarity).

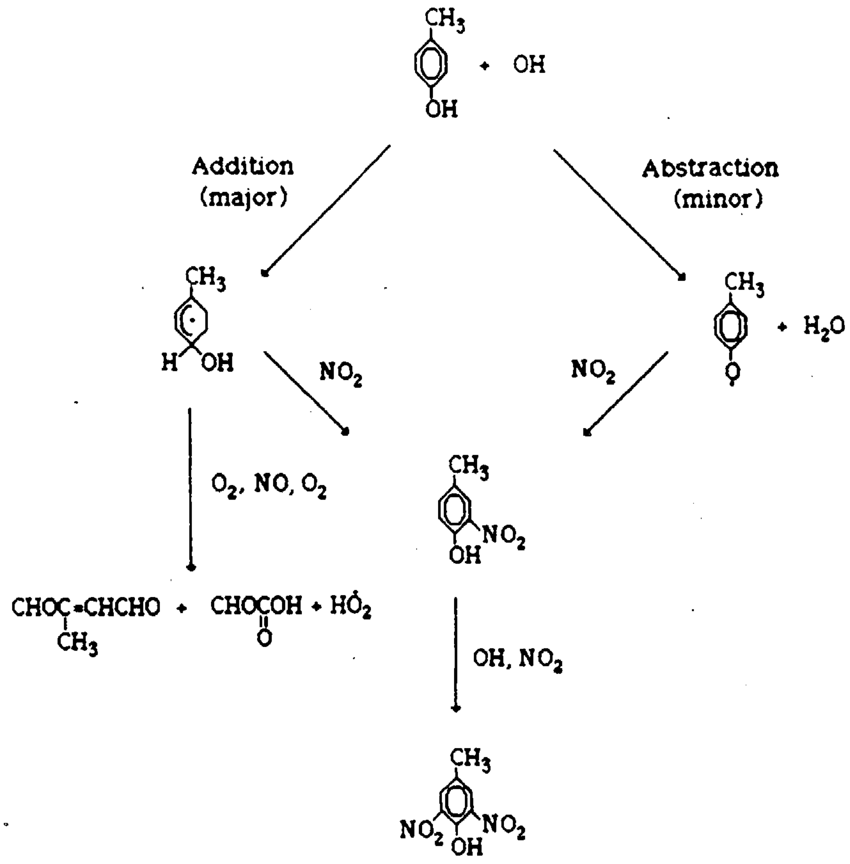


Figure 11.8-7. Para-Cresol Photooxidation Mechanism.

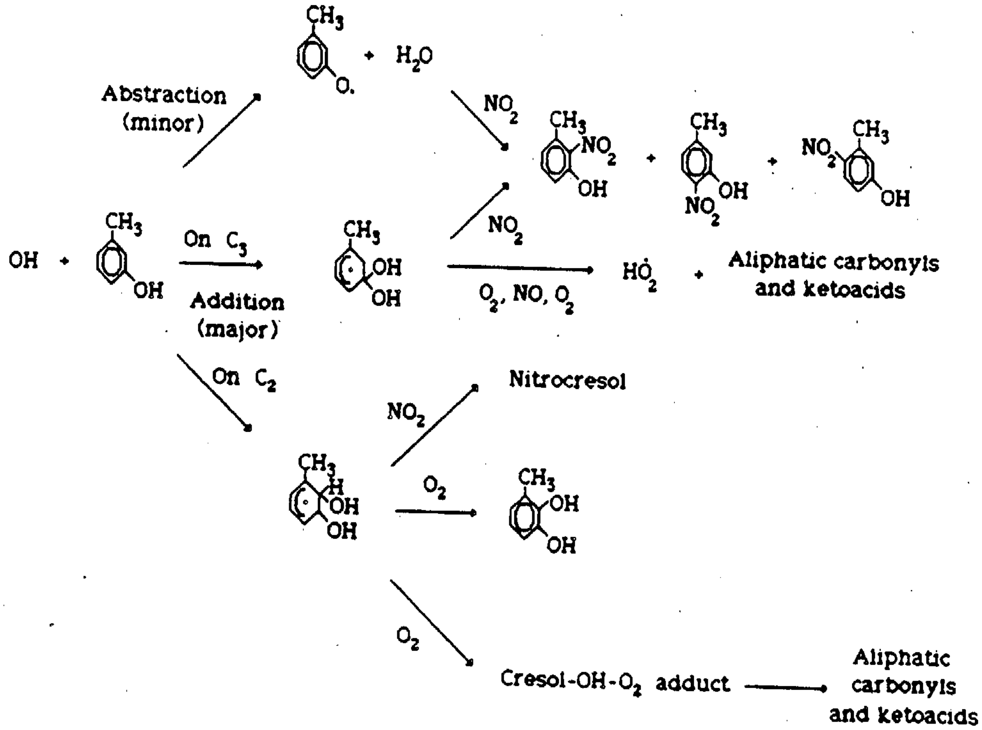


Figure 11.8-8. Meta-Cresol Photooxidation Mechanism.

The OH-initiated oxidation of p-cresol (Figure 11.8-7) should yield only one nitrocresol isomer, 3-nitro-4-hydroxy toluene (2-nitro-4-methyl phenol) and the ring opening products $CHOC(CH_3)=CHCHO$ and CHOCOOH acid). Reaction of the nitrocresol with OH, followed by reaction of either the OH adduct or the phenoxy radical with NO_2, yields one dinitrocresol isomer. Reactions of the ring opening products include photolysis and reaction with OH. Expected products include glyoxal, PAN, CO, CO_2, and free radicals.

In the same way, photooxidation of m-cresol (Figure 11.8-8) should yield several nitrocresols, dicarbonyls, and their reaction products. For this isomer, OH may add on the C_2 carbon as well as on the OH-bearing C_3 carbon. Addition on the C_3 carbon will lead to three nitrocresol isomers and to aliphatic dicarbonyls and ketoacids, this pathway being identical to that of OH reaction with p-cresol. Addition on the C_2 carbon, if any, will lead to three competing pathways of reaction with NO_2, reaction with O_2 by addition, and reaction with O_2 by abstraction (see reactions of toluene-OH adduct in Figure 11.8-1). Reaction with NO_2 will yield one or more nitrocresols. O_2 addition will lead to ring opening and formation of dicarbonyls and ketoacids. O_2 abstraction will lead to a new product, the diphenol 2,3-dihydroxytoluene.

We emphasize again that reaction mechanisms proposed for meta and para-cresol are tentative and await experimental confirmation. Many reactions similar to those discussed in this chapter are also included in Chapter 24, which describes the atmospheric chemistry of phenol and of several nitrophenols.

11.9 REFERENCES

Akimoto, H., M. Hoshino, G. Inoue, M. Okuda and N. Washida. 1978. "Reaction mechanism of the photooxidation of the toluene-NO_2-O_2-N_2 system in the gas phase," Bull. Chem. Soc. Japan 51:2496-2502.

Atkinson, R., W.P.L. Carter, K.R. Darnell, A.M. Winer and J.N. Pitts, Jr. 1980. "A smog chamber and modeling study of the gas phase NO_x-air photooxidation of toluene and the cresols," International Journal of Chemical Kinetics 12:779-836.

Atkinson, R., W.P.L. Carter and A.M. Winer. 1983. "Effects of pressure on product yields in the NO_x photooxidations of selected aromatic hydrocarbons," Journal of Physical Chemistry 87:1605-1610.

Bandow, H., N. Washida and H. Akimoto. 1985. "Ring cleavage reactions of aromatic hydrocarbons studied by FT-IR spectroscopy. I. Photooxidation of toluene and benzene in the NO_x-air system," Bull. Chem. Soc. Japan 58:2531-2540.

Besemer, A.C. 1982. "Formation of chemical compounds from irradiated mixtures of aromatic hydrocarbons and nitrogen oxides," Atmospheric Environment 16:1599-1602.

Dumdei, B.E. and R.J. O'Brien. 1984. "Toluene degradation products in simulated atmospheric conditions," Nature 311:248-250.

Gery, M.W., D.L. Fox, H. Jeffries, L. Stockburger and W.S. Weathers. 1985. "A continuous stirred tank reactor investigation of the gas phase reaction of hydroxyl radicals and toluene," International Journal of Chemical Kinetics 17:931-955.

Gosselin, R.E., H.C. Hodge, R.P. Smith and M.N. Gleason. 1984. Clinical toxicology of commercial products, 5th edition. The Williams and Wilkins Co., Baltimore, MD.

Grosjean, D. 1983. "Atmospheric reactions of pyruvic acid," Atmospheric Environment 17:2379-2382.

Grosjean, D. 1984. "Atmospheric reactions of ortho cresol: gas phase and aerosol products," Atmospheric Environment 18:1641-1652.

Grosjean, D. 1985. "Reactions of o-cresol and nitrocresol with NO_x in sunlight and with ozone-nitrogen dioxide mixtures in the dark," Environmental Science and Technology 19:968-974.

Grosjean, D. and K. Fung. 1984. "Hydrocarbons and carbonyls in Los Angeles air," Journal of the Air Pollution Control Association 34:537-543.

Hill, S. 1985. 1984 toxic use survey: Bay Area Air Quality Management District. Bay Area Air Quality Management District, San Francisco, CA.

Hoshika, Y. and G. Muto. 1978. "Gas-liquid-solid chromatographic determination of phenols in air using Tenax-GC and alkaline precolumns," Journal of Chromatography 157:277-284.

Hoshino, M., H. Akimoto and M. Okuda. 1978. "Photochemical oxidation of benzene, toluene and ethylbenzene initiated by OH radicals in the gas phase," Bull. Chem. Soc. Japan 51:718-724.

Kaufman, C.Y. 1986a. Personal communication from Regulatory Manager, PMC Specialties Group, Inc., Productol Division, Santa Fe Springs, CA (26 August).

Kaufman, C.Y. 1986b. Letter from Regulatory Manager, PMC Specialties Group, Inc., Productol Division, Santa Fe Springs, CA to M. B. Rogozen, SAIC (3 February).

Kenley, R. A., J.E. Davenport and D.G. Hendry. 1981. "Gas phase hydroxyl radical reactions. Products and pathways for reaction of OH with aromatic hydrocarbons," Journal of Physical Chemistry 85:2740-2746.

Leone, J.A., R.C. Flagan, D. Grosjean and J.H. Seinfeld. 1985. "An outdoor smog chamber and modeling study of toluene-NO_x photooxidation," International Journal of Chemical Kinetics 17:177-216.

Leuenberger, C., M.P. Ligocki and J.F. Pankow. 1985. "Trace organic compounds in rain. 4. Identities, concentrations and scavenging mechanisms for phenols in urban air and rain," Environmental Science and Technology 19:1053-1058.

Pellizzari, E.D. 1979. Information on the characteristics of ambient organic vapors in areas of high chemical production. Prepared by Research Triangle Institute for the U.S. Environmental Protection Agency, Research Triangle Park, NC.

SAI (Systems Applications, Inc.). 1980. Human exposure to atmospheric concentration of selected chemicals: Volume 1. Prepared for the U.S. Environmental Protection Agency, Research Triangle Park, NC (NTIS: PB81-193252).

Shepson, P.B., E.O. Edney and E.W. Corse. 1984. "Ring fragmentation reactions on the photooxidations of toluene and o-xylene," Journal of Physical Chemistry 88:4122-4126.

Tonti, T. 1986. Personal communication from Purchasing Agent, Shell Chemical Company, Martinez, CA (26 August).

Tuazon, E.C., R. Atkinson, H. McLeod, H.W. Biermann, A.M. Winer, W.P.L. Carter and J.N. Pitts, Jr. 1984. "Yields of glyoxal and methylglyoxal from the NO_x-air photooxidations of toluene and m- and p-xylene," Environmental Science and Technology 18:981-984.

USDOC (U.S. Department of Commerce) Bureau of Economic Analysis. 1985. OBERS. BEA regional projections, Vol. I. State projections to 2035. U.S. Government Printing Office, Washington, D.C.

Verschueren, K. 1977. Handbook of environmental data on organic chemicals Van Nostrand Reinhold Company, New York, NY.

Weber, R.C., P.A. Parker and M. Bowser. 1981. Vapor pressure distribution of rselected organic chemicals. U.S. Environmental Protection Agency, Industrial Environmental Research Laboratory, Cincinnati, OH, EPA-600/2-81-021.