APPENDIX D

ATMOSPHERIC LIFETIME AND FATE OF EPOXYETHANE

A Report Submitted in Partial Fulfillment of
California Air Resources Board Contract No. A732-107

"Lifetimes and Fates of Toxic Air Contaminants in
California's Atmosphere"

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TABLE OF CONTENTS

		Page
A.	Introduction	D-3
B.	Chemical Loss Processes	D-5
	1. Ozone Reaction	D-5
	2. OH Radical Reaction	D-5
	3. NO_3 Radical Reaction	D-7
	4. Photolysis	D-8
C.	Physical Loss Processes	D-8
D.	Atmospheric Formation Processes	D-9
E.	Atmospheric Lifetimes	D-10
F.	Ambient Concentration	D-11
G.	References	D-11

A. Introduction

The atmospheric fates of chemical compounds emitted into the troposphere are governed by a number of chemical and physical removal processes. As the result of laboratory studies carried out over the past 20 years, the potentially important gas-phase chemical reaction pathways which must be considered includes:

- Photolysis during daylight hours
- Reaction with the hydroxyl (OH) radical during daylight hours
- Reaction with the hydroperoxyl (HO_2) radical, mainly during afternoon/evening hours
- Reaction with the nitrate (NO_3) radical during nighttime hours
- Reaction with nitrogen dioxide (NO_2)
- Reaction with ozone (O_3)
- Reaction with gaseous nitric acid (HNO_3)

For the great majority of organic compounds, the most important of these remain photolysis and reaction with hydroxyl (OH) and nitrate (NO_3) radicals and with ozone (O_3).

However, for a limited number of organic compounds, one or more of the other reactive chemical species in the troposphere may react with organic compounds at significant rates. For example, HO_2 radicals react with formaldehyde and, more slowly, with acetaldehyde and glyoxal; NO_2 reacts with dialkenes; and gaseous HNO_3 reacts with basic compounds such as the amines.

Additionally, for chemical compounds present in the adsorbed phase, photolysis and reaction with O_3, N_2O_5, NO_2, HNO_3, HONO, H_2SO_4 and hydrogen peroxide (H_2O_2) may contribute to their degradation. For certain of these reactions involving adsorbed organics, synergistic interactions may be of importance.

The physical removal processes can be defined in a simplistic manner as accretion (or coagulation) of particles, and dry and wet deposition of gases and particles. Removal of gases and particles at ground surfaces (including snow and other moist surfaces) is referred to as dry deposition, while removal of these species by precipitation is referred to as wet deposition. Our current understanding of these processes, which are

dynamic in nature, must be considered to be semi-quantitative at the present time, and in general there is a lack of experimental data concerning these processes for most organic compounds (Atkinson, 1988; Bidleman, 1988).

The atmospheric lifetime τ of a chemical is defined as the time to decay to a concentration of 1/e (=0.368) of that initially present. Also,

$$\frac{1}{\tau} = \frac{1}{\tau_{\text{chemical}}} + \frac{1}{\tau_{\text{physical}}} \qquad (1)$$

where τ_{chemical} and τ_{physical} are the lifetimes of the chemical with respect to only chemical reaction and only physical loss processes, respectively. These chemical and physical lifetimes are composites of those for the individual loss processes, for example

$$\frac{1}{\tau_{\text{chemical}}} = \frac{1}{\tau_{\text{photolysis}}} + \frac{1}{\tau_{OH}} + \frac{1}{\tau_{NO_3}} + \frac{1}{\tau_{O_3}} \ldots \qquad (2)$$

where $\tau_{\text{photolysis}}$, τ_{OH}, τ_{NO_3} and τ_{O_3} are the lifetimes with respect to photolysis, reaction with tho OH radical, reaction with the NO_3 radical, and reaction with O_3, respectively. In turn, these reactive loss processes are determined by the rate constants, k_x, for reaction and the ambient atmospheric concentrations, [X], of the reactive intermediates. For example

$$\frac{1}{\tau_{OH}} = k_{OH}[OH]$$

For photolysis, the photolysis rate depends on the absorption cross section (σ), the photolysis quantum yield (ϕ), and the radiation intensity (J), all of which are wavelength dependent:

$$\frac{1}{\tau_{\text{photolysis}}} = k_{\text{photolysis}} = \int_{\sim 290\ \text{nm}}^{\sim 800\ \text{nm}} \sigma_\lambda \phi_\lambda J_\lambda \, d\lambda$$

In this report, we describe the available literature data concerning the chemical and physical removal processes for epoxyethane ($CH_2—O—CH_2$) and estimate its resulting atmospheric lifetime. We will also summarize the atmospheric chemistry of this compound. Since epoxyethane is gaseous under atmospheric conditions, we consider only the gas-phase processes.

B. Chemical Loss Processes

1. Ozone Reaction

No experimental data have been reported concerning the gas-phase reaction of O_3 with epoxyethane (Atkinson and Carter, 1984). However, based upon the magnitude of the rate constant for the gas-phase reaction of the OH radical with epoxyethane and the literature data for the reactions of O_3 with saturated organic compounds such as the alkanes and carbonyls not containing >C=C< bonds (Atkinson and Carter, 1984), it is expected that the room temperature rate constant for the reaction of O_3 with epoxyethane will be

$$k(O_3 + \text{epoxyethane}) < 10^{-20} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

at 298 K.

2. OH Radical Reaction

The available kinetic data are given in Table 1. At room temperature, the absolute rate constants of Zetzsch (1980), Lorenz and Zellner (1984) and Wallington et al. (1988) exhibit a spread of a factor of 1.8, but are consistent with the upper limit to the rate constant derived by Klöpffer et al. (1986). The only temperature-dependent study is that of Lorenz and Zellner (1984), who observed a rapid increase in the rate constant above 435 K, leading to marked non-Arrhenius behavior. Atkinson (1989) used a unit-weighted average of the room temperature rate constants of Zetzsch (1980), Lorenz and Zellner (1984) and Wallington et al. (1988) to recommend

$$k(\text{OH} + \text{epoxyethane}) = 7.6 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at 298 K,}$$

with an estimated overall uncertainty of ±50%.

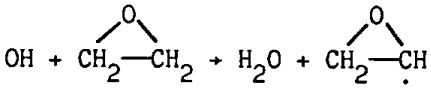
Table 1. Rate Constants k and Temperature-Dependent Parameters, $k = Ae^{-B/T}$, for the Gas-Phase Reaction of the OH Radical with Epoxyethane (from Atkinson, 1989)

$10^{12} \times A$ (cm^3 molecule^{-1} s^{-1})	B (K)	$10^{12} \times k_1$ (cm^3 molecule^{-1} s^{-1})	at T (K)	Technique[a]	Reference
		0.053 ± 0.01	295	FP-RF	Zetzsch (1980)
		0.080 ± 0.016	297	LP-RF	Lorenz and Zellner (1984)
		0.18 ± 0.04	377		
11 ± 4	1460 ± 150 (297-435 K)	0.40 ± 0.08	435		
		1.6 ± 0.1	501		
		2.7 ± 0.5	515		
		<0.10	300	RR [relative to k(propane) $\equiv$ 1.17×10^{-12}][b]	Klöpffer et al. (1986)
		0.095 ± 0.005	296	FP-RF	Wallington et al. (1988)

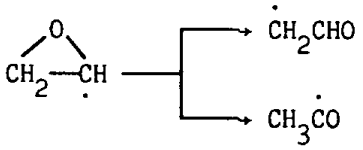
[a] LP ≡ laser photolysis; FP ≡ flash photolysis; RF ≡ resonance fluorescence; RR ≡ relative rate.
[b] Recommendation of Atkinson (1989).

Because of the high magnitude of the temperature dependence measured by Lorenz and Zellner (1984), leading to an Arrhenius pre-exponential factor of 1.2×10^{-11} cm^3 $molecule^{-1}$ s^{-1} for rate data obtained over the range 297-435 K and a markedly higher value for data obtained over the temperature range 435-515 K, no temperature dependence was recommended by Atkinson (1989).

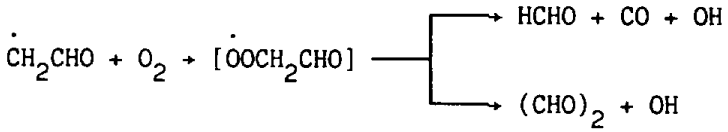
This OH radical reaction almost certainly proceeds by H atom abstraction from the C-H bonds



The initially formed radical is expected to rapidly undergo ring cleavage



Using laser induced fluorescence detection to monitor the vinoxy (CH_2CHO) radical, Lorenz and Zellner (1984) measured CH_2CHO yields at 298 K of 0.08 ± 0.03 and 0.23 ± 0.08 at 10 and 60 Torr total pressure of helium diluent, respectively. The reaction products of the OH radical reaction with epoxyethane under atmospheric conditions are not presently known. [The vinoxy radical reacts rapidly with O_2, with a room temperature rate constant of 2.6×10^{-13} cm^3 $molecule^{-1}$ s^{-1}, with the reaction products possibly being (Gutman and Nelson, 1983; Lorenz et al., 1985)



3. NO_3 Radical Reaction

No data are currently available concerning the gas-phase reaction of the NO_3 radical with epoxyethane. Based on the kinetic data for the corresponding OH radical reaction (see above) and for the gas-phase reactions of the NO_3 radical with alkanes, ethers and alcohols (Wallington et

al., 1986a,b, 1987; Atkinson et al., 1988), it is expected that the room temperature rate constant for the gas-phase reaction of the NO_3 radical with epoxyethane will be

$$k_3(NO_3 + \text{epoxyethane}) < 5 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

at 298 K.

4. Photolysis

Epoxyethane will not undergo photolysis in the actinic region, since epoxyethane does not absorb radiation above 290 nm. The long wavelength limit to the absorption is reported to be at 212 nm (Calvert and Pitts, 1966).

C. Physical Loss Processes

There are no published literature data available concerning dry deposition of epoxyethane. Under California Air Resources Board funding, the Statewide Air Pollution Research Center at the University of California, Riverside, carried out a series of experiments to determine the loss rates of epoxyethane as a function of the water vapor concentration in a 5800 liter Teflon-coated chamber (Winer et al., 1987). Epoxyethane and water vapor concentrations were monitored by in situ long pathlength Fourier transform infrared (FT-IR) absorption spectroscopy. The initial epoxyethane concentrations were ~1.4×10^{14} molecule cm^{-3} (~6 parts-per-million mixing ratio), and all experiments were carried out at 298 ± 2 K.

The experimental conditions and observed loss rates of epoxyethane are given in Table 2. Since the experiment carried out at the lowest relative humidity exhibited the highest epoxyethane loss rate, these data presented in Table 2 show that under these experimental conditions there was no observable hydrolysis of epoxyethane (the small losses of epoxyethane were attributed to a slow removal at the chamber walls). These data yield an upper limit to the loss rate for epoxyethane at ~50% relative humidity and room temperature of $\leq 4 \times 10^{-7}$ s^{-1}, corresponding to a minimum lifetime of epoxyethane due to hydrolysis of 29 days, with the likelihood of a much longer lifetime due to this removal process.

Table 2. Experimental Conditions and Results for the Behavior of Epoxyethane in the Presence of Water Vapor

Diluent Gas	Relative Humidity (%)	Observed Epoxyethane Loss	Loss Rate (s^{-1})
N_2	<1	1.5% over 4 hrs	$\leq 1 \times 10^{-6}$
N_2	49	<0.5% over 2 hrs	$< 7 \times 10^{-7}$
Air	49	4% over 29 hrs	$\leq 4 \times 10^{-7}$

Washout ratios, W, where

$$W = \text{Concentration}_{rain}/\text{Concentration}_{air}$$

have been determined for epoxyethane at 278 K and 288 K (Dana et al., 1985), with values of W = 3.8 at 278 K and 6.2 at 288 K being measured. When these values of W for epoxyethane are compared to the washout ratios of $W = 10^4 - 10^6$ for species which are very efficiently scavenged by rainwater, such as phenol and particles (Eisenreich et al., 1981; Atkinson, 1988), it is clear that epoxyethane is inefficiently removed from the troposphere by wet deposition. Indeed, the values of W for epoxyethane are very similar to those for methylchloroform (CH_3CCl_3) [W ~5 at 298 K (Dana et al., 1985)], for which wet deposition plays no role in its tropospheric removal [the methylchloroform lifetime in the troposphere is 6-7 years, and is due to reaction with the OH radical (Prinn et al., 1987)]. Thus, it is expected that wet deposition will not lead to a significant tropospheric loss rate of epoxyethane.

D. Atmospheric Formation Processes

No chemical formation processes for epoxyethane in the troposphere are expected with the current knowledge of atmospheric chemistry of organic compounds (see, for example, Atkinson and Lloyd, 1984). Two possible reactions leading to formation of epoxyethane in the troposphere are the gas-phase reactions of ethene with the $O(^3P)$ atom and O_3, and at

atmospheric pressure and room temperature and below neither of these reactions leads to the formation of epoxyethane (Atkinson and Lloyd, 1984).

E. Atmospheric Lifetimes

The rate constants, or upper limits thereof, cited above for the gas-phase reactions of OH and NO_3 radicals and O_3 with epoxyethane can be combined with measured or estimated ambient atmospheric concentrations of OH and NO_3 radicals and O_3 to calculate the atmospheric lifetimes of epoxyethane with respect to these potential gas-phase reactions. For this purpose, we use ambient atmospheric concentrations of 1.5×10^6 molecule cm^{-3} for OH radicals during a 12-hr daytime period (Prinn et al., 1987) (an average tropospheric concentration for the northern and southern hemispheres derived from a knowledge of the total worldwide emissions of CH_3CCl_3 and the present atmospheric burden of CH_3CCl_3), 2.4×10^8 molecule cm^{-3} for NO_3 radicals during a 12-hr nighttime period (Platt et al., 1984; Atkinson et al., 1986) and 7×10^{11} molecule cm^{-3} for O_3 during a complete 24-hr day (Logan, 1985). The calculated lifetimes due to these gas-phase reactions are given in Table 3.

Table 3. Calculated Atmospheric Lifetimes of Epoxyethane with Respect to Gas-Phase Room Temperature Reaction with OH and NO_3 Radicals and O_3

Reaction with	Lifetime τ
OH[a]	200 days
NO_3[b]	>5 years
O_3[c]	4.5 years

[a]For a 12-hr average daytime OH radical concentration of 1.5×10^6 molecule cm^{-3} (Prinn et al., 1987).
[b]For a 12-hr average nighttime NO_3 radical concentration of 2.4×10^8 molecule cm^{-3} (Platt et al., 1984; Atkinson et al., 1986).
[c]For a 24-hr average O_3 concentration of 7×10^{11} molecule cm^{-3} [30 ppb] (Logan, 1985).

Clearly, the dominant gas-phase chemical removal process is the reaction with the OH radical, leading to a calculated lifetime of ~200 days. This calculation uses a room temperature rate constant for the OH radical reaction; use of a rate constant for the OH radical reaction at the temperatures applicable to the mid-troposphere (~270 K) would lead to a longer calculated lifetime of ~300 days. With a lifetime of epoxyethane of this magnitude, wet deposition is expected to be of no significance as a tropospheric removal process, and the overall lifetime of epoxyethane is calculated to be in the range 200-300 days. With a lifetime of this magnitude, epoxyethane will be distributed over a global scale.

F. Ambient Concentration

To our knowledge, no ambient air data have been reported in the literature for epoxyethane.

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APPENDIX E

ATMOSPHERIC LIFETIME AND FATE OF FORMALDEHYDE

A Report Submitted in Partial Fulfillment of
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TABLE OF CONTENTS

		Page
A.	Introduction	E-3
B.	Chemical Loss Processes	E-5
	1. Reaction with Ozone	E-5
	2. Reaction with the Hydroxyl Radical	E-5
	3. Reaction with the NO_3 Radical	E-11
	4. Reaction with the HO_2 Radical	E-13
	5. Photolysis	E-14
C.	Physical Loss Processes	E-16
D.	Tropospheric Lifetime of Formaldehyde	E-18
E.	Atmospheric Formation of HCHO	E-19
F.	Ambient Atmospheric Concentrations of HCHO	E-21
G.	Conclusions	E-23
H.	References	E-23

A. Introduction

The atmospheric fates of chemical compounds emitted into the troposphere are governed by a number of chemical and physical removal processes. As the result of laboratory studies carried out over the past 20 years, the potentially important gas-phase chemical reaction pathways which must be considered includes:

- Photolysis during daylight hours.
- Reaction with the hydroxyl (OH) radical during daylight hours.
- Reaction with the hydroperoxyl (HO_2) radical, mainly during afternoon/evening hours.
- Reaction with the nitrate (NO_3) radical during nighttime hours.
- Reaction with nitrogen dioxide (NO_2).
- Reaction with ozone (O_3).
- Reaction with gaseous nitric acid (HNO_3).

For the great majority of organic compounds, the most important of these remain photolysis and reaction with hydroxyl (OH) and nitrate (NO_3) radicals and with ozone (O_3).

However, for a limited number of organic compounds, one or more of the other reactive chemical species in the troposphere may react with organic compounds at significant rates. For example, HO_2 radicals react with formaldehyde (see Section B.4, below) and, more slowly, with acetaldehyde and glyoxal; NO_2 reacts with dialkenes; and gaseous HNO_3 reacts with basic compounds such as the amines.

Additionally, for chemical compounds present in the adsorbed phase, photolysis and reaction with O_3, N_2O_5, NO_2, HNO_3, HONO, H_2SO_4 and hydrogen peroxide (H_2O_2) may contribute to their degradation. For certain of these reactions involving adsorbed organics, synergistic interactions may be of importance.

The physical removal processes can be defined in a simplistic manner as accretion (or coagulation) of particles, and dry and wet deposition of gases and particles. Removal of gases and particles at ground surfaces (including snow and other moist surfaces) is referred to as dry deposition, while removal of these species by precipitation is referred to as wet deposition. Our current understanding of these processes, which are

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$$\frac{1}{\tau} = \frac{1}{\tau_{\text{chemical}}} + \frac{1}{\tau_{\text{physical}}} \qquad (1)$$

where $\tau_{chemical}$ and $\tau_{physical}$ are the lifetimes of the chemical with respect to only chemical reaction and only physical loss processes, respectively. These chemical and physical lifetimes are composites of those for the individual loss processes, for example

$$\frac{1}{\tau_{\text{chemical}}} = \frac{1}{\tau_{\text{photolysis}}} + \frac{1}{\tau_{OH}} + \frac{1}{\tau_{NO_3}} + \frac{1}{\tau_{O_3}} \cdots \qquad (2)$$

where $\tau_{photolysis}$, τ_{OH}, τ_{NO_3} and τ_{O_3} are the lifetimes with respect to photolysis, reaction with the OH radical, reaction with the NO_3 radical, and reaction with O_3, respectively. In turn, these reactive loss processes are determined by the rate constants, k_x, for reaction and the ambient atmospheric concentrations, [X], of the reactive intermediates. For example

$$\frac{1}{\tau_{OH}} = k_{OH}[OH]$$

For photolysis, the photolysis rate depends on the absorption cross section (σ), the photolysis quantum yield (ϕ), and the radiation intensity (J), all of which are wavelength dependent:

$$\frac{1}{\tau_{\text{photolysis}}} = k_{\text{photolysis}} = \int_{\sim 290\text{ nm}}^{\sim 800\text{ nm}} \sigma_\lambda \phi_\lambda J_\lambda \, d\lambda$$

In this report, the available literature data concerning the chemical and physical removal processes for formaldehyde (HCHO) are presented and its resulting atmospheric lifetime is estimated. The atmospheric chemistry of this compound is also discussed. Although formaldehyde is gaseous at room temperature, its dissolution into the aqueous phase and subsequent aqueous-phase reactions must also be considered in addition to the gas-phase processes.

B. Chemical Loss Processes

1. Reaction with Ozone

The only kinetic data for the gas-phase reaction of O_3 with HCHO is the upper limit to the rate constant of $k_1 \leq 2.1 \times 10^{-24}$ cm^3 $molecule^{-1}$ s^{-1} obtained by Braslavsky and Heicklen (1976) at 298 K. This upper limit to the rate constant is consistent with the small amount of rate constant data for the other saturated aldehydes CH_3CHO, $(CHO)_2$ and CH_3COCHO (Atkinson and Carter, 1984).

2. Reaction with the Hydroxyl Radical

The available literature data concerning the kinetics and mechanism of the reaction of the OH radical with HCHO have been reviewed and evaluated by Atkinson (1989). The available rate constant data are given in Table 1. The rate constants obtained by Hoare (1962, 1966), Baldwin and Cowe (1962), Blundell et al. (1965), Westenberg and Fristrom (1966), Hoare and Peacock (1966), Morris and Niki (1971a,b), Peeters and Mahnen (1973), Vandooren and Van Tiggelen (1977), Niki et al. (1978), Atkinson and Pitts (1978), Stief et al. (1980), Temps and Wagner (1984) and Zabarnick et al. (1988) for $^{12}CH_2O$ and of Niki et al. (1984) for $^{13}CH_2O$ are plotted in Arrhenius form in Figure 1. A significant amount of scatter in these data is evident. Since the rate constant for the self reaction of OH radicals is subject to significant uncertainties (DeMore et al., 1987), the rate constants derived from the study of Smith (1978) are not plotted in Figure 1 and were not used by Atkinson (1989) in the evaluation of the rate constant for this reaction.

It can be seen from Figure 1 that the rate constant for this reaction appears to be approximately independent of temperature over the range ~230-500 K, but that at temperatures >500 K the rate constant increases with increasing temperature. At around room temperature, absolute rate

Table 1. Rate Constants k_2 and Temperature-Dependent Parameters ($k_2 = Ae^{-B/T}$) for the Gas-Phase Reaction of the OH Radical with Formaldehyde

$10^{12} \times A$ (cm^3 molecule^{-1} s^{-1})	B (K)	$10^{12} \times k_2$ (cm^3 molecule^{-1} s^{-1})	at T (K)	Technique	Reference
Formaldehyde					
		28 ± 8	773	RR [relative to $k(CH_4) = 6.95 \times 10^{-18} T^2 e^{-1282/T}$]^a	Hoare (1962)
		29	798		
		33	873		
		33	923		
		47	813	RR [relative to $k(H_2) = 1.12 \times 10^{-12}$]^a	Baldwin and Cowe (1962)
		26 ± 3	773	RR [relative to $k(CH_4) = 7.91 \times 10^{-13}$]^a	Blundell et al. (1965)
~880	~4265		1250-1400	RR [relative to $k(CO) = 1.12 \times 10^{-13} e^{0.000907T}$]^a	Westenberg and Fristrom (1965)
		25	723	RR [relative to $k(CH_4) = 6.95 \times 10^{-18} T^2 e^{-1282/T}$]^a	Hoare (1966)
		29	798		
		33	923		
		25	798	RR [relative to $k(CH_4) = 8.88 \times 10^{-13}$]^a	Hoare and Peacock (1966)
		14	798	RR [relative to $k(C_2H_6) = 5.07 \times 10^{-12}$]^a	Hoare and Peacock (1966)

Table 1 (continued) - 2

10^{12} x A (cm^3 molecule^{-1} s^{-1})	B (K)	10^{12} x k_2 (cm^3 molecule^{-1} s^{-1})	at T (K)	Technique	Reference
		≥6.6	300	DF-MS	Herron and Penzhorn (1969)
		14 ± 3.5	298	DF-MS	Morris and Niki (1971a)
		15.3	298	DF-MS	Morris and Niki (1971b)
	~500	42	1600	Flame-MS	Peeters and Mahnen (1973)
		17	485	Flame-MS	Vandooren and Van Tiggelen (1977)
		22	570		
		15.8 ± 0.9	298 ± 2	RR [relative to k(ethene-d_4) = 8.78 x 10^{-12}]^a	Niki et al. (1978)
		9.4 ± 1.0	299.3	FP-RF	Atkinson and Pitts (1978)
		9.4 ± 1.0	356.5		
12.5	88 ± 151	10.3 ± 1.1	426.4		
		5.5 ± 0.7	268	DF-MS [relative to	Smith (1978)
		5.5 ± 0.7	298	$k(OH + OH) = 4.2 \times 10^{-12} e^{-240/T}$]^b	
		7.4 ± 1.0	334		
		11.22 ± 0.98	228	FP-RF	Stief et al. (1980)
		10.28 ± 0.90	257		
		9.86 ± 1.13	298		
10.5 ± 1.1	0	10.46 ± 1.50	362		
		8.1 ± 1.7	296	DF-LMR	Temps and Wagner (1984)

Table 1 (continued) - 3

10^{12} x A (cm^3 molecule^{-1} s^{-1})	B (K)	10^{12} x k_2 (cm^3 molecule^{-1} s^{-1})	at T (K)	Technique	Reference
		10.7 ± 1.3	296	LP-LIF	Zabarnick et al. (1988)
		12.5 ± 0.5	297		
		11.4 ± 0.6	297		
		13.6 ± 1.0	297		
		13.2 ± 0.4	298		
		13.1 ± 0.4	298		
		13.7 ± 0.5	299		
		12.0 ± 0.3	301		
		13.9 ± 0.4	378		
		13.3 ± 0.3	473		
		11.4 ± 0.5	567		
		15.8 ± 1.2	572		
		14.1 ± 0.5	574		
16.6 ± 2.0	86 ± 40	16.7 ± 0.8	576		
Formaldehyde-^{13}C		8.40 ± 0.51	299 ± 2	RR [relative to k(ethene) = 8.48×10^{-12}][a]	Niki et al. (1984)
Formaldehyde-d_1		~14	298	DF-MS	Morris and Niki (1971a)

[a]From Atkinson (1989).

[b]From DeMore et al. (1987).

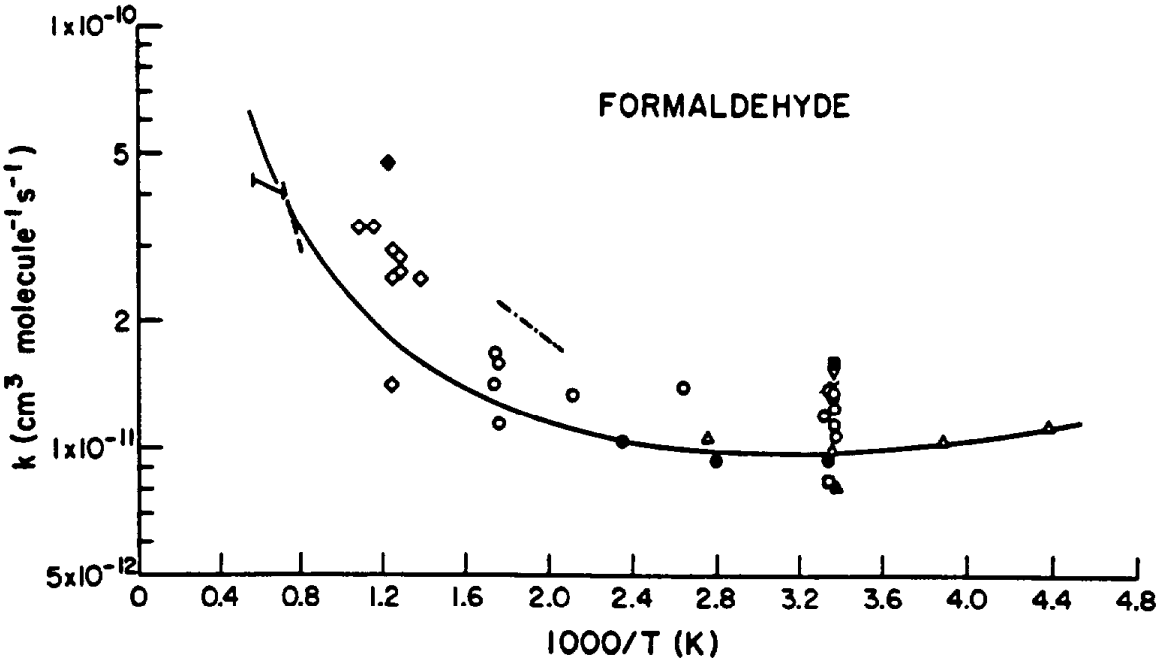

Figure 1. Arrhenius plot of rate constants for the reaction of the OH radical with formaldehyde. (◇) Hoare (1962, 1966), Blundell et al. (1965), Hoare and Peacock (1966); (◆) Baldwin and Cowe (1962); (— — —) Westenberg and Fristrom (1965); (x) Morris and Niki (1971a); (▽) Morris and Niki (1971b); (⊢⊣) Peeters and Mahnen (1973); (—·—·—) Vandooren and Van Tiggelen (1977); (■) Niki et al. (1978); (●) Atkinson and Pitts (1978); (△) Stief et al. (1980); (▲) Temps and Wagner (1984); (○) Zabarnick et al. (1988); (□) Niki et al. (1984) [for reaction with formaldehyde-^{13}C]; (——) recommendation (see text).

constants have been determined by Morris and Niki (1971a), Atkinson and Pitts (1978), Stief et al. (1980), Temps and Wagner (1984) and Zabarnick et al. (1988). Again, a significant amount of scatter is observed, with Morris and Niki (1971a) and Zabarnick et al. (1988) obtaining rate constants of (1.2-1.4) x 10^{-11} cm^3 $molecule^{-1}$ s^{-1}, Atkinson and Pitts (1978) and Stief et al. (1980) rate constants of (9.4-9.9) x 10^{-12} cm^3 $molecule^{-1}$ s^{-1}, and Temps and Wagner (1984) a rate constant of 8.1 x 10^{-12} cm^3 $molecule^{-1}$ s^{-1}.

Based upon the data shown in Figure 1, the Arrhenius plot exhibits significant curvature. A unit-weighted least-squares analysis of the absolute rate constants determined by Atkinson and Pitts (1978) and Stief et al. (1980) (which are in excellent agreement) was carried out by Atkinson (1989), using the expression $k_2 = CT^2e^{-D/T}$, to obtain the recommendation of

$$k_2(HCHO) = (1.25^{+0.20}_{-0.18}) \times 10^{-17}\ T^2\ e^{(648 \pm 45)/T}\ cm^3\ molecule^{-1}\ s^{-1}$$

over the temperature range 228-426 K, where the indicated errors are two least-squares standard deviations, and

$$k_2(HCHO) = 9.77 \times 10^{-12}\ cm^3\ molecule^{-1}\ s^{-1}$$

at 298 K, with an estimated overall uncertainty at 298 K of ±30%. This recommendation is ~10% higher than that recommended by Atkinson (1986) of $k_2(HCHO) = 9.0 \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1}, independent of temperature over the same range of 228-426 K. At elevated temperatures, the recommended expression yields calculated rate constants in good agreement with those obtained from the flame studies of Westenberg and Fristrom (1965) and Peeters and Mahnen (1973) [Figure 1].

As expected, the rate constant for the reaction of OH radicals with formaldehyde-^{13}C is, within the likely experimental errors, essentially identical to that for formaldehyde-^{12}C (Niki et al., 1984).

This OH radical reaction with formaldehyde can proceed by the pathways

$$OH + HCHO \rightarrow HCO + H_2O \quad (2a)$$

$$\rightarrow HCOOH + H \quad (2b)$$

$$\rightarrow H + CO + H_2O \quad (2c)$$

Morrison and Heicklen (1980), Temps and Wagner (1984) and Niki et al. (1984) have shown from product studies that reaction pathway (2b) is negligible, accounting for $\lesssim$2% of the overall reaction (Niki et al., 1984). Morrison and Heicklen (1980) did not observe any formation (<10%) of HCOOH, and concluded that reaction pathways (2a) and (2c) occur with approximately equal probability. More recently, Temps and Wagner (1984), using a discharge flow technique with LMR detection to monitor both OH and HCO radicals, have shown that reaction pathway (2a) accounts for 100±5% of the overall reaction. Thus, at room temperature the OH radical reaction with formaldehyde proceeds essentially entirely by the H-atom abstraction process.

$$OH + HCHO \rightarrow H_2O + HCO$$

The resulting HCO radical reacts rapidly with O_2 to yield the HO_2 radical (DeMore et al., 1987; Atkinson et al., 1989):

$$HCO + O_2 \rightarrow HO_2 + CO$$

3. Reaction with the NO_3 Radical

Kinetic data for the gas-phase reaction of the NO_3 radical with HCHO have been obtained by Atkinson et al. (1984), Cantrell et al. (1985) and Hjorth et al. (1988). All of these studies, except for five experiments in the study of Cantrell et al. (1985), were relative rate measurements carried out at room temperature, with the rate constants for the NO_3 radical reaction with HCHO being relative to the equilibrium constant K for the reactions

$$NO_3 + NO_2 \underset{}{\overset{M}{\rightleftharpoons}} N_2O_5$$

While the reported rate constants k_3 range from (3.2-6.3) x 10^{-16} cm^3 $molecule^{-1}$ s^{-1}, at least part of these differences are due to the differing values of K used. The available rate data are given in Table 2, with the relative rate data from Atkinson et al. (1984), Cantrell et al. (1985) and Hjorth et al. (1988) being re-evaluated by use of an equilibrium constant of K = 1.26 x 10^{-27} $e^{11275/T}$ cm^3 $molecule^{-1}$ (K = $[N_2O_5]/[NO_2][NO_3]$]). The (re-evaluated) relative rate constant of Atkinson et al. (1984) agrees very well with the rate constant obtained from the absolute rate measurements of Cantrell et al. (1985), while the re-evaluated rate constants derived from the relative rate data of Cantrell et al. (1985) and Hjorth et al. (1988) are 30-50% higher.

Table 2. Room Temperature Rate Constants, k_3, for the Gas-Phase Reaction of the NO_3 Radical with Formaldehyde

10^{16} x k_3 (cm^3 $molecule^{-1}$ s^{-1})	at T (K)	Reference
5.9 ± 0.5[a]	298 ± 1	Atkinson et al. (1984)
5.6[b] / 8.9 ± 0.7[a]	298 ± 2	Cantrell et al. (1985)
7.9 ± 1.6[a]	295 ± 2	Hjorth et al. (1988)

[a]Relative to an equilibrium constant of K = 1.26 x 10^{-27} $e^{11275/T}$ cm^3 $molecule^{-1}$, derived from the experimental data of Burrows et al. (1985), Tuazon et al. (1984), Kircher et al. (1984) and Cantrell et al. (1988).

[b]NO_3 radicals monitored directly, leading to an absolute rate measurement.

Both of the recent NASA (DeMore et al., 1987) and IUPAC (Atkinson et al., 1989) data evaluations recommend a rate constant for the reaction of the NO_3 radical with HCHO of 6.0×10^{-16} cm^3 $molecule^{-1}$ s^{-1} at 298 K, with an estimated uncertainty of ± a factor of 1.5-2. Moreover, the room temperature rate constant for the reaction of the NO_3 radical with CH_3CHO also determined by Atkinson et al. (1984), when re-evaluated as discussed above, is in excellent agreement with the recent absolute rate constant of Dlugokencky and Howard (1989). Accordingly, the rate constant for the reaction of the NO_3 radical with HCHO is taken to be $k_3 = 6 \times 10^{-16}$ cm^3 $molecule^{-1}$ s^{-1} at 298 K. As for the OH radical reaction, this reaction proceeds by H-atom abstraction

$$NO_3 + HCHO \rightarrow HNO_3 + HCO$$

4. Reaction with the HO_2 Radical

The HO_2 radical has been shown to react with HCHO (Su et al., 1979a,b; Niki et al., 1980a,b; Veyret et al., 1982, 1989; Barnes et al., 1985), with this reaction proceeding by initial HO_2 radical addition to form the $HOOCH_2\dot{O}$ species

$$HO_2 + HCHO \rightarrow HOOCH_2\dot{O}$$

This alkoxy radical then rapidly undergoes isomerization via a 5-membered transition state to the peroxy radical $HOCH_2O\dot{O}$

$$HOOCH_2\dot{O} \rightarrow \dot{O}OCH_2OH$$

Furthermore, the available data show that this sequence of reactions is reversible, and hence that the reactions to be considered are

$$HO_2 + HCHO \underset{(-4)}{\overset{(4)}{\rightleftarrows}} [HOOCH_2\dot{O}] \underset{(-4)}{\overset{(4)}{\rightleftarrows}} \dot{O}OCH_2OH \qquad (4,-4)$$

The rate constants for the forward [reaction (4)] and back [reaction (-4)] reactions are given in Table 3. Clearly, the reported rate data span a significant range, especially for reaction (-4). The most recent IUPAC data evaluation (Atkinson et al., 1989) utilizes the rate constants of Barnes et al. (1985) and Veyret et al. (1989) to recommend that

$$k_4 = 9.7 \times 10^{-15} e^{625/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

$$= 7.9 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K}$$

and

$$k_{-4} = 2.4 \times 10^{12} e^{-7000/T} \text{ s}^{-1}$$

$$= 150 \text{ s}^{-1} \text{ at } 298 \text{ K}.$$

Since HO_2 radicals react rapidly with NO (DeMore et al., 1987; Atkinson et al., 1989), and the other reaction of the $HOCH_2OO$ radical [in addition to reaction (-4)] is expected to be with NO,

$$HOCH_2O\dot{O} + NO \rightarrow HOCH_2\dot{O} + NO_2$$

the magnitude of the rate constant for decomposition of the $HOCH_2O\dot{O}$ radical [reaction (-4)] means that the reaction of the HO_2 radical with HCHO is of minor importance as a tropospheric loss process for HCHO.

5. Photolysis

The absorption cross sections and quantum yields for the photolysis of HCHO have most recently been reviewed and evaluated by DeMore et al. (1987) and Atkinson et al. (1989). The most recent IUPAC evaluation (Atkinson et al., 1989) accepts the absorption cross-section data of Moortgat et al. (1983). At the longer wavelengths, these absorption cross-sections of Moortgat et al. (1983) are higher than those measured by Bass et al. (1980), but are substantiated by recent unpublished data of H. W. Biermann (University of California, Riverside). The recommended absorption cross-sections and quantum yields (Atkinson et al., 1989) for the processes

$$HCHO + h\nu \rightarrow H + HCO \qquad (5a)$$

$$HCHO + h\nu \rightarrow H_2 + CO \qquad (5b)$$

are tabulated in Table 4.

Table 3. Rate Constants k_4 and k_{-4} for the Gas-Phase Reaction of the HO_2 Radical with Formaldehyde [$HO_2 + HCHO \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} OOCH_2OH$]

$10^{14} \times k_4$ (cm^3 $molecule^{-1}$ s^{-1})	k_{-4} (s^{-1})	at T (K)	Reference
1.0	1.5	298 ± 2	Su et al. (1979a,b)
7.5 ± 3.5	30	298	Veyret et al. (1982)
11 ± 4	20^{+20}_{-10}	273	Barnes et al. (1985)
$0.77\ e^{(625 \pm 550)/T}$	$2.0 \times 10^{12}\ e^{-(7000 \pm 2000)/T}$	275-333	Veyret et al. (1989)
6.0 ± 0.7	100 ± 50	295	

Table 4. Absorption Cross Sections, σ, and Quantum Yields, ϕ, for the Photolysis of HCHO (from Atkinson et al., 1989)

λ (nm)	10^{20} σ(cm^2)[a] 298 K	ϕ_{5a}	ϕ_{5b}
270	0.95	0.38	0.43
280	1.80	0.57	0.32
290	2.93	0.73	0.24
300	4.06	0.78	0.21
310	4.60	0.78	0.22
320	4.15	0.62	0.38
330	3.21	0.27	0.66
340	2.22	0	0.56[b]
350	1.25	0	0.21[b]
360	0.18	0	0.03[b]

[a]The values are averaged for 10 nm intervals centered on the indicated wavelength.

[b]760 torr total pressure of air.

C. Physical Loss Processes

In addition to the tropospheric chemical loss processes of HCHO discussed above, HCHO is soluble in water and is hence incorporated into cloud, rain and fog water, with subsequent aqueous phase reactions (see, for example, Graedel and Weschler, 1981; Jacob and Hoffmann, 1983; Munger et al., 1983, 1986; Adewuyi et al., 1984; Jacob, 1986; McElroy, 1986; Graedel et al., 1986; Pandis and Seinfeld, 1989). In the aqueous phase, formaldehyde is present as the glycol through the reaction

$$HCHO(aq) + H_2O(aq) \rightleftarrows H_2C(OH)_2(aq)$$

with this equilibrium almost totally favoring the glycol (Jacob, 1986), with $[H_2C(OH)_2aq]/[HCHO(aq)] = 2.3 \times 10^3$ at 298 K (Betterton and Hoffmann, 1988).

Betterton and Hoffmann (1988) measured the apparent Henry's law coefficient, H^*, where

$$H^* = \{[HCHO(aq)] + [H_2C(OH)_2(aq)]\}/[HCHO(gas)]$$

as a function of temperature over the range 288-318 K. At 298 K the value of H^* determined was $H^* = (3.0 \pm 0.7) \times 10^3$ mol atm^{-1}.

For gas-phase organic compounds which are very efficiently rained out (and for particles, which are also very efficiently rained out), the washout ratio W, where W = concentration in rain/concentration in air ($W = RTH^*$ with the definition of H^* given above), is 10^5 to 10^6 (Eisenreich et al., 1981; Atkinson, 1988). The value of H^* of Betterton and Hoffmann (1988) corresponds to a washout ratio of $W = 7.3 \times 10^4$ at 298 K. With a washout ratio of this magnitude, wet deposition of HCHO is expected to be significant as a tropospheric loss process for HCHO during rain or fog events.

Incorporation of HCHO into rain, cloud and fog water is followed by a series of aqueous-phase reactions, including the oxidation of formaldehyde to formic acid (see, for example, Jacob, 1986; Pandis and Seinfeld, 1989).

$$OH(aq) + H_2C(OH)_2(aq) \xrightarrow{O_2} HCOOH(aq) + HO_2(aq) + H_2O$$

$$H_2C(OH)_2(aq) + O_3(aq) \rightarrow \text{products}$$

Furthermore, the complexation of sulfur [S(IV)] to hydroxymethanesulfonate

$$HSO_3^-(aq) + HCHO(aq) \rightarrow HOCH_2SO_3^-(aq)$$

$$SO_3^{2-}(aq) + HCHO(aq) \rightarrow HOCH_2SO_3^-(aq) + OH^-(aq)$$

leads to stabilization of S(IV) in clouds under nighttime conditions. In the presence of light, the reaction of aqueous OH radicals with hydroxymethanesulfonate

$$OH(aq) + HOCH_2SO_3^-(aq) \rightarrow HCHO(aq) + SO_3^-(aq) + H_2O$$

is expected to be reasonably rapid, leading to a lifetime of hydroxymethanesulfonate in cloudwater of the order of 30 min (Jacob, 1986).

The solubility of HCHO in water leads to efficient wet deposition of HCHO, with gas-phase HCHO being expected to be efficiently scavenged into rain, cloud and fog water. This wet deposition process is, of course, episodic, and will, on average, lead to a tropospheric lifetime of HCHO somewhat shorter than calculated solely from the gas-phase loss processes discussed above (see below).

D. Tropospheric Lifetime of Formaldehyde

As discussed above, the tropospheric lifetime of HCHO is determined from the loss rates of both the chemical and physical loss processes. Based upon the rate constants given above for the gas-phase reactions of HCHO with OH, NO_3 and HO_2 radicals and with O_3, and measured or estimated tropospheric concentrations of these reactive species of: OH radicals, 1.5×10^6 molecule cm^{-3} during daylight hours (Prinn et al., 1987); NO_3 radicals, 2.4×10^8 molecule cm^{-3} during nighttime hours (Platt et al., 1984; Atkinson et al., 1986); HO_2 radicals, $\sim 10^7$ molecule cm^{-3} (Hard et al., 1984; Zellner and Weibring, 1989); and O_3, 7×10^{11} molecule cm^{-3} throughout a 24-hr period (Logan, 1985), the tropospheric loss rates of HCHO due to these chemical processes can be calculated. The calculated lifetimes due to these individual reactions are then: reaction with the OH radical, 1.6 days; reaction with the NO_3 radical, 160 days; reaction with the HO_2 radical (neglecting the back-decomposition reaction of the $HOOCH_2\dot{O}$ radical), ~15 days; and reaction with O_3, $>2 \times 10^4$ years. Since the back-decomposition of the $HOCH_2O\dot{O}$ radical formed from the HO_2 radical reaction significantly decreases the importance of the HO_2 radical reaction as an HCHO loss process [by around two orders of magnitude for 2×10^{11} molecule cm^{-3} (10 ppb) of NO], the above calculated lifetime of HCHO due to reaction with the HO_2 radical reaction is likely to be of minor importance as a tropospheric loss process.

Clearly, the daytime OH radical reaction is the dominant of these chemical reaction loss processes. Photolysis of HCHO is estimated to lead to a lifetime (due to photolysis) of 0.4 day in the lower troposphere for a zenith angle of 40^o (Atkinson, 1988; W. P. L. Carter, University of California, Riverside, private communication, 1989). Thus, photolysis and

reaction with the OH radical are the major tropospheric chemical loss processes, with an overall lifetime of HCHO of ~0.3 days and with photolysis being the dominant removal route. Wet deposition will, on average, lead to a shorter tropospheric lifetime, but since wet deposition is episodic in nature, the above lifetime calculated from OH radical reaction and photolysis is best regarded as being the tropospheric lifetime, with faster removal of HCHO from the lower troposphere during rain and/or fog events. It must also be noted that photolysis and reaction with the OH radical only occur during daytime hours.

E. Atmospheric Formation of HCHO

Formaldehyde is formed in the troposphere from the tropospheric degradation reactions of many organic compounds. In the "clean" troposphere, HCHO is formed as a product of the atmospheric reactions of methane:

$$OH + CH_4 \rightarrow H_2O + \dot{C}H_3$$

$$\dot{C}H_3 + \rightarrow CH_3\dot{O}$$

[involving rapid formation of CH_3O_2, followed by reactions of the methyl peroxy radical with NO, NO_2, HO_2 radicals and other organic peroxy radicals to ultimately lead to formation of the methoxy ($CH_3\dot{O}$ radical (Ravishankara, 1988; Atkinson, 1990)], followed by the reaction

$$\dot{C}H_3O + O_2 \rightarrow HCHO + HO_2$$

The formation of $CH_3\dot{O}$ and/or $\dot{C}H_3$ radicals during the atmospheric degradation reactions of organic compounds thus leads to the formation of HCHO. Sources of $\dot{C}H_3$ radicals include the important tropospheric reactions of acetaldehyde

$$CH_3CHO + h\nu \rightarrow \dot{C}H_3 + HCO$$

$$OH + CH_3CHO \rightarrow H_2O + CH_3\dot{C}O$$

$$\downarrow O_2$$

$$CH_3C(O)OO^{\cdot}$$

$$NO \rightarrow NO_2$$

$$\dot{C}H_3 + CO_2$$

and the decomposition reactions of the more complex alkoxy radicals; for example

$$(CH_3)_3C\dot{O} \rightarrow CH_3COCH_3 + \dot{C}H_3$$

Analogous decompositions of alkoxy radicals can also lead directly to HCHO. For example, the β-hydroxyalkoxy radicals formed after OH radical addition to the terminal alkenes (such as the $CH_3CHOHCH_2O^{\cdot}$ radical formed from propene) decompose, at least in part, as follows:

$$CH_3CHOHCH_2\dot{O} \rightarrow CH_3\dot{C}HOH + HCHO$$

The simplest α-hydroxy radical, $\dot{C}H_2OH$, which is formed from the decomposition reactions of $R_1R_2C(\dot{O})CH_2OH$ β-hydroxyalkoxy radicals, reacts rapidly with O_2 to yield HCHO and the HO_2 radical (Atkinson and Lloyd, 1984; DeMore et al., 1987; Atkinson et al., 1989)

$$\dot{C}H_2OH + O_2 \rightarrow HCHO + HO_2$$

In addition, the gas-phase reactions of O_3 with alkenes containing terminal $=CH_2$ groups lead to the formation of HCHO. For example, for the reaction of O_3 with ethene at room temperature and atmospheric pressure of air (Atkinson and Lloyd, 1984; Atkinson and Carter, 1984; Atkinson, 1990)

$$O_3 + CH_2=CH_2 \rightarrow HCHO + 0.37\ \dot{C}H_2O\dot{O} + 0.12\ HO_2 + 0.13\ H_2 + 0.19\ CO_2 + 0.44\ CO + 0.44\ H_2O$$

with similar HCHO yields for other 1-alkenes (Atkinson, 1990).

Thus, in polluted airmasses characteristic of urban areas, the atmospheric formation of HCHO from organic precursors occurs. Grosjean et al. (1983) concluded from ambient measurements that in many cases the atmospheric formation of HCHO dominates over direct emission of HCHO from combustion sources. More recent ambient air monitoring data in the Los Angeles air basin (Lawson et al. 1990) provide clear evidence for directly emitted HCHO as well as HCHO formed in the atmosphere by photochemical reactions of organic precursors. However, Lawson et al. (1990) also conclude that the atmospheric formation of HCHO dominates over direct emissions of HCHO under conditions of high photochemical activity in the Los Angeles air basin.

F. Ambient Atmospheric Concentrations of HCHO

The measured HCHO mixing ratio in the clean lower troposphere is around 0.2 parts-per-billion (ppb) [Lowe et al., 1981; Lowe and Schmidt, 1983], with these measured mixing ratios being in good agreement with the predicted values of 0.25-0.35 ppb presented by Logan et al. (1981) for the lower troposphere in the northern hemisphere. Reported data for the ambient concentrations of HCHO in California since 1980 are given in Table 5. These particular data were all collected in the Los Angeles air basin, and vary from <1 ppb up to 86 ppb, with the most recent concentrations measured in the California Air Resources Board-funded intercomparison studies at Claremont and Glendora in the Los Angeles air basin being significantly lower, ≤25 ppb (Grosjean, 1988; Lawson et al. 1990). Further, as yet unpublished, ambient HCHO data are available from the 1987 ARB-funded South Coast Air Quality Study (SCAQS).

It may be expected that the ambient atmospheric HCHO levels encountered in the Los Angeles air basin are among the highest to be expected in California, and hence the ambient atmospheric HCHO mixing ratios in California range from a few tenths of a part-per-billion (for clean tropospheric air) up to a few tens of ppb, with the actual values depending to a large extent on the organic precursor emissions, the extent of photochemical activity and the meteorological conditions pertaining.

Table 5. Recent Measurements of Formaldehyde Concentrations in Ambient Air in California

HCHO Mixing Ratio (ppb)	Measurement Date and Place	Reference
2-40	5-6/1980, Los Angeles	Grosjean (1982)
3-48	9-10/1980, Claremont	Grosjean (1982)
10-41	7/1980, Riverside	Singh et al. (1982)
18-60	7-10/1980, Los Angeles	Grosjean et al. (1983)
65-70	7-8/1980, Burbank	Grosjean et al. (1983)
53	7/1980, Pasadena	Grosjean et al. (1983)
5	8/1980, Pacoima	Grosjean et al. (1983)
33	8/1980, Newhall	Grosjean et al. (1983)
38-47	9-10/1980, Rosemead	Grosjean et al. (1983)
27	9/1980, Covina	Grosjean et al. (1983)
42	9/1980, Cucamonga	Grosjean et al. (1983)
59-66	10/1980, El Monte	Grosjean et al. (1983)
34	10/1980, San Dimas	Grosjean et al. (1983)
34	10/1980, Upland	Grosjean et al. (1983)
0.7-35	10/1980, Azusa	Grosjean et al. (1983)
0.5-40	10/1980, Lennox	Grosjean et al. (1983)
4-86	9-11/1981, Los Angeles	Grosjean and Fung (1984)
1.5-11	9/1985, Claremont	Grosjean (1988)
3-22	8/1986, Glendora	Lawson et al. (1990)

G. Conclusions

Formaldehyde is both directly emitted into the atmosphere as well as being formed in the atmosphere from the photochemical degradation of more methane and other non-methane organic compounds. HCHO is removed from the lower troposphere mainly by photolysis and reaction with the OH radical, and by wet deposition (leading to incorporation of formaldehyde into rain, cloud and fog water). The estimated lifetime of HCHO due to photolysis and OH radical reaction is ~0.3 days, with episodic wet deposition events leading to shorter lifetimes. Reported ambient atmospheric HCHO concentrations in the Los Angeles air basin (expected to have among the higher levels encountered in California) range up 86 ppb, with mixing ratios measured during two recent intercomparison studies in 1985 and 1986 ranging up to 25 ppb.

H. References

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APPENDIX F

ATMOSPHERIC LIFETIME AND FATE OF ACETALDEHYDE

A Report Submitted in Partial Fulfillment of
California Air Resources Board Contract No. A732-107

"Lifetimes and Fates of Toxic Air Contaminants in
California's Atmosphere"

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TABLE OF CONTENTS

		Page
A.	Introduction	F-3
B.	Chemical Loss Processes	F-5
	1. Reaction with Ozone	F-5
	2. Reaction with the Hydroxyl Radical	F-5
	3. Reaction with the NO_3 Radical	F-9
	4. Reaction with the HO_2 Radical	F-11
	5. Photolysis	F-12
C.	Physical Loss Processes	F-13
D.	Tropospheric Lifetime and Fate of Acetaldehyde	F-14
E.	Atmospheric Formation of Acetaldehyde	F-19
F.	Ambient Atmospheric Concentrations of CH_3CHO	F-21
G.	Conclusions	F-22
H.	References	F-23

A. Introduction

The atmospheric fates of chemical compounds emitted into the troposphere are governed by a number of chemical and physical removal processes. As the result of laboratory studies carried out over the past 20 years, the potentially important gas-phase chemical reaction pathways which must be considered includes:

- Photolysis during daylight hours.
- Reaction with the hydroxyl (OH) radical during daylight hours.
- Reaction with the hydroperoxyl (HO_2) radical, mainly during afternoon/evening hours.
- Reaction with the nitrate (NO_3) radical during nighttime hours.
- Reaction with nitrogen dioxide (NO_2).
- Reaction with ozone (O_3).
- Reaction with gaseous nitric acid (HNO_3).

For the great majority of organic compounds, the most important of these remain photolysis and reaction with hydroxyl (OH) and nitrate (NO_3) radicals and with ozone (O_3).

However, for a limited number of organic compounds, one or more of the other reactive chemical species in the troposphere may react with organic compounds at significant rates. For example, HO_2 radicals react with formaldehyde and, more slowly, with acetaldehyde and glyoxal; NO_2 reacts with dialkenes; and gaseous HNO_3 reacts with basic compounds such as the amines.

Additionally, for chemical compounds present in the adsorbed phase, photolysis and reaction with O_3, N_2O_5, NO_2, HNO_3, HONO, H_2SO_4 and hydrogen peroxide (H_2O_2) may contribute to their degradation. For certain of these reactions involving adsorbed organics, synergistic interactions may be of importance.

The physical removal processes can be defined in a simplistic manner as accretion (or coagulation) of particles, and dry and wet deposition of gases and particles. Removal of gases and particles at ground surfaces (including snow and other moist surfaces) is referred to as dry deposition, while removal of these species by precipitation is referred to as wet deposition. Our current understanding of these processes, which are

dynamic in nature, must be considered to be semi-quantitative at the present time, and in general there is a lack of experimental data concerning these processes for most organic compounds (Atkinson, 1988; Bidleman, 1988).

The atmospheric lifetime τ of a chemical is defined as the time to decay to a concentration of 1/e (=0.368) of that initially present. Also,

$$\frac{1}{\tau} = \frac{1}{\tau_{\text{chemical}}} + \frac{1}{\tau_{\text{physical}}} \qquad (1)$$

where $\tau_{chemical}$ and $\tau_{physical}$ are the lifetimes of the chemical with respect to only chemical reaction and only physical loss processes, respectively. These chemical and physical lifetimes are composites of those for the individual loss processes, for example

$$\frac{1}{\tau_{\text{chemical}}} = \frac{1}{\tau_{\text{photolysis}}} + \frac{1}{\tau_{OH}} + \frac{1}{\tau_{NO_3}} + \frac{1}{\tau_{O_3}} \ldots \qquad (2)$$

where $\tau_{photolysis}$, τ_{OH}, τ_{NO_3} and τ_{O_3} are the lifetimes with respect to photolysis, reaction with the OH radical, reaction with the NO_3 radical, and reaction with O_3, respectively. In turn, these reactive loss processes are determined by the rate constants, k_x, for reaction and the ambient atmospheric concentrations, [X], of the reactive intermediates. For example

$$\frac{1}{\tau_{OH}} = k_{OH}[OH]$$

For photolysis, the photolysis rate depends on the absorption cross section (σ), the photolysis quantum yield (ϕ), and the radiation intensity (J), all of which are wavelength dependent:

$$\frac{1}{\tau_{photolysis}} = k_{photolysis} = \int_{\sim 290\ nm}^{\sim 800\ nm} \sigma_\lambda \phi_\lambda J_\lambda \, d\lambda$$

In this report, the available literature data concerning the chemical and physical removal processes for acetaldehyde (CH_3CHO) are presented and its resulting atmospheric lifetime is estimated. The atmospheric chemistry of this compound is also discussed. Although acetaldehyde is gaseous at room temperature, its dissolution into the aqueous phase and subsequent aqueous-phase reactions must also be considered in addition to the gas-phase processes.

B. Chemical Loss Processes

1. Reaction with Ozone

Rate constants for the gas-phase reaction of O_3 with acetaldehyde have been reported by Stedman and Niki (1973) and Atkinson et al. (1981). Both studies were carried out at room temperature using essentially the same experimental technique. However, the rate constants obtained differ substantially, with Stedman and Niki (1973) reporting a rate constant of $k_1 = (3.4 \pm 0.5) \times 10^{-20}$ cm^3 molecule^{-1} s^{-1} at 298 ± 2 K and Atkinson et al. (1981) an upper limit to the rate constant of $k_1 \leq 6 \times 10^{-21}$ cm^3 molecule^{-1} s^{-1} at 296 ± 2 K. Since only upper limits to the room temperature rate constants of $k < 10^{-20}$ cm^3 molecule^{-1} s^{-1} have been obtained for the aldehydes HCHO, $(CHO)_2$ and CH_3COCHO (Atkinson and Carter, 1984), Atkinson and Carter (1984) recommended that

$$k_1(CH_3CHO) < 1 \times 10^{-20} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K}$$

2. Reaction with the Hydroxyl Radical

The available literature data concerning the kinetics and mechanism of the reaction of the OH radical with HCHO have been reviewed and evaluated by Atkinson (1989). The available kinetic data are given in Table 1, and those of Morris et al. (1971), Morris and Niki (1971), Niki et al. (1978), Atkinson and Pitts (1978), Kerr and Sheppard (1981), Semmes et al. (1985) and Michael et al. (1985) are plotted in Arrhenius form in Figure 1. Within the cited experimental errors, the room

Table 1. Rate Constants k_2 and Temperature-Dependent Parameters ($k_2 = Ae^{-B/T}$) for the Gas-Phase Reaction of the OH Radical with Acetaldehyde

$10^{12} \times A$ (cm^3 molecule^{-1} s^{-1})	B (K)	$10^{12} \times k_2$ (cm^3 molecule^{-1} s^{-1})	at T (K)	Technique	Reference
		15 ± 3.8	300	DF-MS	Morris et al. (1971)
		15.3	298	DF-MS	Morris and Niki (1971)
		≤18	295 ± 2	RR [relative to k(HONO) = 4.80×10^{-12}][a]	Cox et al. (1976)
		≥3.0	1100	RR [relative to k(CO) = 3.04×10^{-13}][a]	Colket et al. (1977)
		16.2 ± 1.8	298 ± 2	RR [relative to k(ethene) = 8.52×10^{-12}][a]	Niki et al. (1978)
		16.0 ± 1.6	299.4	FP-RF	Atkinson and Pitts (1978)
		14.4 ± 1.5	355.0		
6.87	-257 ± 151	12.4 ± 1.3	426.1		
		12.8 ± 4.3	298 ± 4	RR [relative to k(ethene) = 8.52×10^{-12}][a]	Kerr and Sheppard (1981)
		14.0 ± 3.1	253	FP-RF	Semmes et al. (1985)
		12.2 ± 2.7	298		
		10.7 ± 2.3	356		
7.1 ± 0.2	-165 ± 91	11.0 ± 2.3	424		
		21.0 ± 1.4	244	DF-RF	Michael et al. (1985)
		19.2 ± 0.6	244		
		18.9 ± 1.4	259		
		17.9 ± 1.2	259		
		15.6 ± 0.8	273		
		16.3 ± 1.2	273		
		17.8 ± 0.6	273		
		19.6 ± 1.2	273		
		14.2 ± 1.0	298		
		14.7 ± 2.8	298		
		13.0 ± 1.2	333		
		14.0 ± 0.8	355		
		14.0 ± 0.4	367		
		14.3 ± 1.0	367		
		15.0 ± 1.0	373		
		11.6 ± 0.6	393		
		11.7 ± 0.8	420		
		10.6 ± 0.6	424		
		11.0 ± 0.6	433		
		11.5 ± 0.8	466		
		10.4 ± 0.4	468		
		10.4 ± 0.8	492		
		9.2 ± 1.4	499		
5.52 ± 0.80	-307 ± 52	9.9 ± 0.4	528		

[a]From Atkinson (1989).

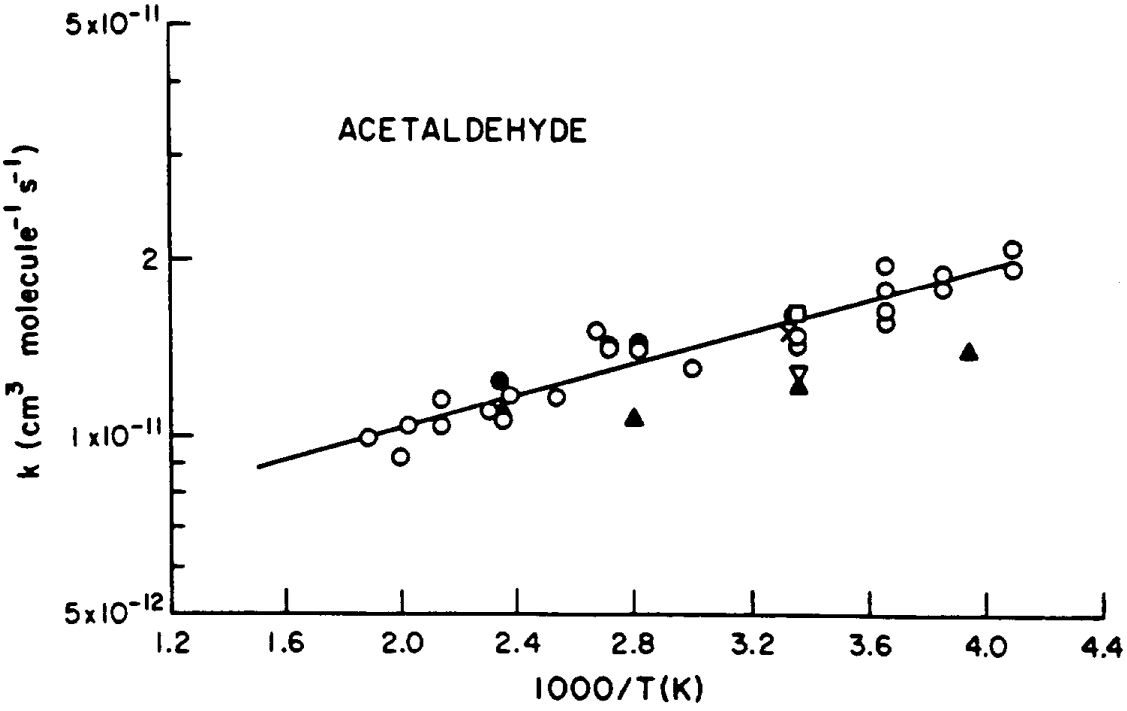


Figure 1. Arrhenius plot of rate constants for the reaction of the OH radical with acetaldehyde. (x) Morris et al., (1971) and Morris and Niki (1971); (□) Niki et al. (1978); (●) Atkinson and Pitts (1978); (▽) Kerr and Sheppard, (1981); (▲) Semmes et al., (1985); (○) Michael et al., (1985); (———) recommendation (see text).

temperature rate constants of Morris et al. (1971), Morris and Niki (1971), Niki et al. (1978), Atkinson and Pitts (1978), Kerr and Sheppard (1981), Semmes et al. (1985) and Michael et al. (1985) are in reasonably good agreement, although those of Kerr and Sheppard (1981) and Semmes et al. (1985) are somewhat lower than the remaining data. The Arrhenius plot (Fig. 1) does not show any definitive evidence of curvature, and hence the experimental data were fitted by Atkinson (1989) to the Arrhenius expression $k = Ae^{-B/T}$. A unit-weighted least-squares analysis of the rate constants of Niki et al. (1978), Atkinson and Pitts (1978) and Michael et al. (1985) leads to the recommendation of

$$k_2(CH_3CHO) = (5.55^{+0.76}_{-0.66}) \times 10^{-12}\ e^{(311 \pm 42)/T}\ cm^3\ molecule^{-1}\ s^{-1}$$

over the temperature range 244-528 K, where the indicated errors are two least-squares standard deviations, and

$$k_2(CH_3CHO) = 1.58 \times 10^{-11}\ cm^3\ molecule^{-1}\ s^{-1}$$

at 298 K, with an estimated overall uncertainty at 298 K of ±20%.

Using the three-parameter expression $k = CT^2e^{-D/T}$, a unit-weighted least-squares analysis of these same kinetic data (Niki et al., 1978; Atkinson and Pitts, 1978; Michael et al., 1985) yields

$$k_2(CH_3CHO) = (6.03^{+1.07}_{-0.92}) \times 10^{-18}\ T^2\ e^{(999 \pm 54)/T}\ cm^3\ molecule^{-1}\ s^{-1}$$

over the temperature range 244-528 K, where the indicated errors are again the two least-squares standard deviations, and

$$k_2(CH_3CHO) = 1.53 \times 10^{-11}\ cm^3\ molecule^{-1}\ s^{-1}$$

at 298 K. Over a wider temperature range extending to temperatures $\gtrsim$600 K, curvature in the Arrhenius plot is expected, and the above three-parameter expression should probably then be used.

The recent rate constants of Semmes et al. (1985) were not included in the evaluation of this rate constant since they reported difficulties in adequately determining the acetaldehyde concentrations in their reactant mixtures.

While definite product and mechanistic data are not available for the OH radical reaction with acetaldehyde, the observation of peroxyacetyl nitrate (PAN) from the reaction of the OH radical with CH_3CHO in air in the presence of NO_x (Atkinson and Lloyd, 1984) shows that at room temperature this reaction must proceed via overall H-atom abstraction from the -CHO group.

$$OH + CH_3CHO \rightarrow H_2O + CH_3\dot{C}O$$

$$CH_3\dot{C}O + O_2 \xrightarrow{M} CH_3C(O)OO\cdot$$

$$CH_3C(O)OO\cdot + NO_2 \rightleftarrows CH_3C(O)OONO_2$$

(PAN)

This is consistent with the observation that the room temperature rate constants for the $\gtrsim C_2$ aldehydes are reasonably similar, increasing only slightly with the length of the alkyl side chain (Atkinson, 1989) and showing that the alkyl substituent group has only a minimal effect on the OH radical rate constant. As for formaldehyde, the observed negative temperature dependence suggests that, although the reaction proceeds by overall H-atom abstraction, the reaction involves initial OH radical addition followed by rapid decomposition of the adduct to the observed products. H-atom abstraction from the $-CH_3$ group is expected to be of minimal importance at room temperature, (Atkinson, 1987).

3. Reaction with the NO_3 Radical

Kinetic data for the gas-phase reaction of the NO_3 radical with CH_3CHO have been obtained by Morris and Niki (1974), Atkinson et al. (1984), Cantrell et al. (1986) and Dlugokencky and Howard (1989). The studies of Morris and Niki (1974), Atkinson et al. (1984) and Cantrell et

al. (1986) were relative rate measurements carried out at room temperature, with the rate constants for the NO_3 radical reaction with CH_3CHO being relative to the equilibrium constant K for the reactions

$$NO_3 + NO_2 \underset{}{\overset{M}{\rightleftharpoons}} N_2O_5$$

The study of Dlugokencky and Howard (1989) was an absolute measurement carried out using a flow system with laser-induced fluorescence detection of the NO_3 radical. The available rate data are given in Table 2, with the relative rate data from Morris and Niki (1974), Atkinson et al. (1984) and Cantrell et al. (1986) being re-evaluated by use of an equilibrium constant of $K = 1.26 \times 10^{-27} e^{11275/T}$ cm^3 $molecule^{-1}$ ($K = [N_2O_5]/\{[NO_2][NO_3]\}$).

These re-evaluated room temperature rate constants of Morris and Niki (1974), Atkinson et al. (1984) and Cantrell et al. (1986) are in good agreement and are in excellent agreement with the absolute room temperature rate constant determined by Dlugokencky and Howard (1989). Since the room temperature rate constants derived from the relative rate studies (Morris and Niki, 1974; Atkinson et al., 1984; Cantrell et al., 1986) have significant uncertainties associated with them because of the uncertainties in the equilibrium constant K for the $NO_3 + NO_2 \rightleftharpoons N_2O_5$ reactions, the absolute data of Dlugokencky and Howard (1989) are used to obtain the recommendation of

$$k_3(CH_3CHO) = 1.4 \times 10^{-12} e^{-1860/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 264 - 274 K, and

$$k_3(CH_3CHO) = 2.7 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at 298 K.}$$

The recent IUPAC evaluation (Atkinson et al., 1989) recommends an identical rate expression.

As is the case for the OH radical reaction, this NO_3 radical reaction proceeds by H atom abstraction from the -CHO group (Cantrell et al., 1986)

$$NO_3 + CH_3CHO \rightarrow HNO_3 + CH_3\dot{C}O$$

Table 2. Room Temperature Rate Constants, k_3, for the Gas-Phase Reaction of the NO_3 Radical with Acetaldehyde

$10^{15} \times k_3$ (cm^3 $molecule^{-1}$ s^{-1})	at T (K)	Reference
2.54 ± 0.64[a]	300	Morris and Niki (1974)
2.44 ± 0.52[a]	298 ± 1	Atkinson et al. (1984)
3.06 ± 0.59[a]	299 ± 1	Cantrell et al. (1986)
1.26 ± 0.15	264	Dlugokencky and Howard (1989)[b]
2.74 ± 0.33	298	
5.27 ± 0.63	332	
10.0 ± 1.2	374	

[a]Relative to an equilibrium constant of $K = 1.26 \times 10^{-27} e^{11275/T}$ cm^3 $molecule^{-1}$, which is derived from the experimental data of Tuazon et al. (1984), Kircher et al. (1984), Burrows et al. (1985) and Cantrell et al. (1988).

[b]NO_3 radicals monitored directly by laser induced fluorescence, with a temperature dependence of $k_3 = 1.44 \times 10^{-12} e^{-(1860 \pm 300)/T}$ cm^3 $molecule^{-1}$ s^{-1}.

4. Reaction with the HO_2 Radical

While the gas-phase reaction of the HO_2 radical with formaldehyde is well documented (see, for example, Atkinson et al., 1989), less definitive data are available concerning the rate constant and reaction products of the analogous HO_2 radical reaction with CH_3CHO. Moortgat and McQuigg (1984) used Fourier transform infrared absorption spectroscopy to study the photooxidation of CH_3CHO in air, and ascribed the formation of CH_3COOH to the reaction of the HO_2 radical with CH_3CHO. The initially formed $CH_3CH(OOH)\dot{O}$ radical was expected to rapidly isomerize (Moortgat and McQuigg, 1984),

$$HO_2 + CH_3CHO \rightarrow [CH_3CH(OOH)\dot{O}] \rightarrow CH_3CH(O\dot{O})OH \qquad (4,-4)$$

followed by

$$2\ CH_3CH(O\dot{O})OH \rightarrow 2\ CH_3CH(\dot{O})OH + O_2$$

$$CH_3CH(\dot{O})OH + O_2 \rightarrow CH_3COOH + HO_2$$

Based upon the time-concentration profiles of the reactants and products and unpublished rate data of Barnes and coworkers for a series of α-dicarbonyls, Moortgat and McQuigg (1984) derived a rate constant for the reaction of HO_2 with CH_3CHO at 298 K of $k_4 = 1 \times 10^{-15}$ cm^3 $molecule^{-1}$ s^{-1}, and a rate constant for the unimolecular decomposition of the $CH_3CH(OOH)\dot{O}$ radical back to reactants of $k_{-4} = 1.5$ s^{-1}. Moortgat and McQuigg (1984) also cited an unpublished rate constant of Barnes and coworkers of $k_4 = 1 \times 10^{-17}$ cm^3 $molecule^{-1}$ s^{-1} for the HO_2 radical reaction with CH_3CHO, based upon the decay rate of HO_2 in the presence of CH_3CHO. However, reformation of the reactants from the initially formed $CH_3CH(OOH)\dot{O}$ radical [reaction (-4)] would lead to this measured rate constant being a lower limit to that for the initial addition reaction.

Moortgat and coworkers (Moortgat et al., 1987) have carried out further studies of the photolysis of CH_3CHO, and derived rate constants at 298 K of $k_4 = 1 \times 10^{-15}$ cm^3 $molecule^{-1}$ s^{-1} and $k_{-4} = 100$ s^{-1}. With these rate constants, the reaction of the HO_2 radical with CH_3CHO is not expected to be a significant loss process for CH_3CHO under tropospheric conditions (see Section D below).

5. Photolysis

The absorption cross-sections and quantum yields for the photolysis of CH_3CHO have most recently been reviewed and evaluated by the IUPAC data panel (Atkinson et al., 1989). This evaluation accepts the earlier evaluation of Baulch et al. (1984). The recommended absorption cross-sections were obtained from the experimental measurements of Calvert and Pitts (1966) and Weaver et al. (1976/77). The recommended quantum yields for the processes,

$$CH_3CHO + h\nu \rightarrow CH_4 + CO \qquad (5a)$$

$$CH_3CHO + h\nu \rightarrow \dot{C}H_3 + HCO \qquad (5b)$$

derived from the studies of Horowitz and Calvert (1982), Horowitz et al. (1982) and Meyrahn et al. (1982), are given in Table 3 together with the recommended absorption cross-sections. At wavelengths >290 nm the other possible photodissociation processes

$$CH_3CHO + h\nu \rightarrow H + CH_3\dot{C}O \qquad (5c)$$

$$CH_3CHO + h\nu \rightarrow H_2 + CH_2CO \qquad (5d)$$

are of negligible importance (Atkinson and Lloyd, 1984; Baulch et al., 1984).

C. Physical Loss Processes

Acetaldehyde can also dissolve in aqueous solutions, and hence the possibility that CH_3CHO is incorporated into cloud, rain and fog water, with subsequent aqueous-phase reactions, needs to be considered. As discussed by Betterton and Hoffmann (1988), CH_3CHO can exist in aqueous solution as the hydrated, gem-diol, form

$$CH_3CHO(aq) + H_2O(aq) \rightleftarrows CH_3CH(OH)_2(aq)$$

Betterton and Hoffmann (1988) measured the apparent Henry's law coefficient, H^*, where

$$H^* = \{[CH_3CHO(aq)] + [CH_3CH(OH)_2(aq)]\}/[CH_3CHO(gas)]$$

as a function of temperature over the range 278-308 K. At 298 K the value of H^* determined was $H^* = 11.4 \pm 0.4$ mol atm^{-1}. The degree of hydration for CH_3CHO is fairly small, with (Betterton and Hoffmann, 1988) $K_{hyd} = [CH_3CH(OH)_2(aq)]/[CH_3CHO(aq)] = 1.4$ at 298 K (which can be contrasted to formaldehyde, for which $K_{hyd} = 2.3 \times 10^3$ at 298 K).

For gas-phase organic compounds which are very efficiently rained out (and for particles, which are also very efficiently rained out), the washout ratio W, where W = concentration in rain/concentration in air ($W = RTH^*$ with the definition of H^* given above), is 10^5 to 10^6 (Eisenreich et al., 1981; Atkinson, 1988). The value of H^* of Betterton and Hoffmann

Table 3. Absorption Cross Sections, σ, and Quantum Yields Φ (for 1 atm air) for the Photolysis of CH_3CHO (from Atkinson et al., 1989)

Wavelength λ (nm)	$10^{20}\sigma$ (cm^2)	Φ_{5_a}	Φ_{5_b}
260	2.0	0.46	0.31
270	3.4	0.31	0.39
280	4.5	0.05	0.58
290	4.9	0.01	0.53
295	4.5	0.00	0.48
300	4.3		0.43
305	3.4		0.37
315	2.1		0.17
320	1.8		0.10
325	1.1		0.04
330	0.69		0.00
335	0.38		
340	0.15		
345	0.08		

(1988) corresponds to a washout ratio of W = 280 at 298 K, in good agreement with the value of 370 reported earlier by Buttery et al. (1969). With a washout ratio of this magnitude, wet deposition of CH_3CHO is expected to be of minor significance as a tropospheric loss process for CH_3CHO, especially compared to the gas-phase processes.

D. Tropospheric Lifetime and Fate of Acetaldehyde

As discussed above, the tropospheric lifetime of CH_3CHO is determined from the loss rates of both the chemical and physical loss processes. Based upon the rate constants given above for the gas-phase reactions of CH_3CHO with OH, NO_3 and HO_2 radicals and with O_3, and measured or estimated tropospheric concentrations of these reactive species of: OH radicals, 1.5×10^6 molecule cm^{-3} during daylight hours (Prinn et al., 1987); NO_3 radicals, 2.4×10^8 molecule cm^{-3} during nighttime hours (Platt et al., 1984; Atkinson et al., 1986); HO_2 radicals, $\simeq 10^7$ molecule cm^{-3} for conditions applicable to polluted areas (Hard et al., 1984; Zellner and Weibring, 1989); and O_3, 7×10^{11} molecule cm^{-3} throughout a 24-hr period

(Logan, 1985), the tropospheric loss rates of CH_3CHO due to these chemical processes can be calculated. The calculated lifetimes due to these individual reactions are then: reaction with the OH radical, 12 hours (i.e., 1 day since the OH radical reaction occurs only during daylight); reaction with the NO_3 radical, 35 days; reaction with the HO_2 radical (neglecting the back-decomposition reaction of the $CH_3CH(OOH)O^{\cdot}$ radical), ~3 years; and reaction with O_3, >4.5 years. Since the back-decomposition of the $CH_3CH(OOH)O^{\cdot}$ radical formed from the HO_2 radical reaction significantly decreases the importance of the HO_2 radical reaction as a CH_3CHO loss process, the above calculated lifetimes of CH_3CHO due to reaction with the HO_2 radical and with O_3 show that these reactions will be totally negligible as a tropospheric loss process for CH_3CHO. Clearly, the daytime OH radical reaction is the dominant of these chemical loss processes.

Photolysis of CH_3CHO is estimated to lead to a lifetime (due to photolysis) of ~6.6 day (~80 hrs) in the lower troposphere for a zenith angle of 0° (Horowitz and Calvert, 1982; Meyrahn et al., 1982). Thus, reaction with the OH radical and, to a lesser extent, photolysis are the major tropospheric chemical loss processes, with an overall lifetime of CH_3CHO of ~12 hours (or 1 day) and with the OH radical reaction being the dominant removal route. Wet deposition will, on average, lead to a shorter tropospheric lifetime, but since wet deposition is episodic in nature, and expected to be of minor importance due to the relatively low washout ratio, the above lifetime calculated from the OH radical reaction can be regarded as being the tropospheric lifetime, with a somewhat faster removal of CH_3CHO from the lower troposphere during rain and/or fog events (see Grosjean and Wright, 1983). It must also be noted that reaction with the OH radical and photolysis only occur during daytime hours.

The reactions subsequent to the OH radical reaction are as discussed below. The initial H atom abstraction reaction

$$OH + CH_3CHO \rightarrow H_2O + CH_3\dot{C}O$$

forms the acetyl radical, which rapidly (and exclusively under tropospheric conditions) adds O_2 to yield the acetyl peroxy radical (Atkinson, 1990).

$$CH_3\dot{C}O + O_2 \xrightarrow{M} CH_3C(O)OO^{\cdot}$$

The acetyl peroxy radical reacts with NO and NO_2

$$CH_3C(O)OO^{\cdot} + NO \rightarrow CH_3C(O)\dot{O} + NO_2$$

$$\Big\downarrow \text{ fast}$$

$$\dot{C}H_3 + CO_2$$

$$CH_3C(O)OO^{\cdot} + NO_2 \underset{\ddagger}{\xrightarrow{M}} CH_3C(O)OONO_2$$

(PAN)

with rate constants of ~5.1 x 10^{-12} $e^{200/T}$ cm^3 $molecule^{-1}$ s^{-1} (1.0 x 10^{-11} cm^3 $molecule^{-1}$ s^{-1} at 298 K) and ~7.2 x 10^{-12} cm^3 $molecule^{-1}$ s^{-1} (at 298 K and 760 Torr total pressure of air), respectively (Atkinson, 1990). Additionally, in the "clean" troposphere, the reactions of the $CH_3C(O)OO^{\cdot}$ radical with HO_2 and $CH_3\dot{O}_2$ radicals may be important,

$$HO_2 + CH_3C(O)OO^{\cdot} \rightarrow CH_3C(O)OOH + O_2 \qquad (a)$$

$$\rightarrow CH_3COOH + O_3 \qquad (b)$$

$$CH_3O_2^{\cdot} + CH_3C(O)OO^{\cdot} \rightarrow CH_3O^{\cdot} + CH_3C(O)O^{\cdot} + O_2 \qquad (c)$$

$$\Big\downarrow \text{ fast}$$

$$\dot{C}H_3 + CO_2$$

$$\rightarrow HCHO + CH_3COOH + O_2 \qquad (d)$$

with k_a/k_b ~3 (Niki et al., 1985) and $k_c \sim k_d \simeq 5.5 \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1} at 298 K (Moortgat et al., 1989). The $\dot{C}H_3$ radical produced in reaction pathway (c) and from the reaction of the $CH_3C(O)OO^{\cdot}$ radical with NO ultimately forms HCHO (Ravishankara, 1988; Atkinson, 1990) by the

following series of reactions

$$\dot{C}H_3 + O_2 \xrightarrow{M} CH_3O_2^{\cdot}$$

$$CH_3O_2^{\cdot} + NO \rightarrow CH_3O^{\cdot} + NO_2$$

$$CH_3O_2^{\cdot} + HO_2 \rightarrow CH_3OOH + O_2$$

$$CH_3OOH + h\nu \rightarrow CH_3O^{\cdot} + OH$$

$$OH + CH_3OOH \rightarrow H_2O + CH_3O_2^{\cdot}$$

$$CH_3O^{\cdot} + O_2 \rightarrow HCHO + HO_2$$

Peroxyacetyl nitrate (PAN) acts as a temporary reservoir of the $CH_3C(O)O\dot{O}$ radical, with a lifetime with respect to thermal decomposition of ~33 min at 298 K and 760 Torr total pressure of air (Atkinson et al., 1989; Atkinson, 1990).

$$CH_3C(O)OONO_2 \xrightarrow{M} CH_3C(O)OO^{\cdot} + NO_2$$

As noted above, PAN formation occurs by the reaction of the acetyl peroxy radical with NO_2, and the organic precursor to PAN formation is the acetyl radical, $CH_3\dot{C}O$. The $CH_3\dot{C}O$ radical is formed from the OH and NO_3 radical reactions with acetaldehyde,

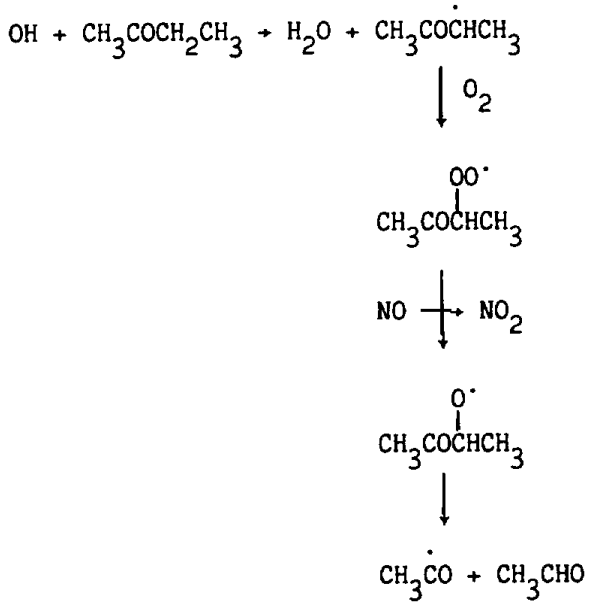
$$\left.\begin{matrix} OH \\ NO_3 \end{matrix}\right\} + CH_3CHO \rightarrow CH_3\dot{C}O + \left\{\begin{matrix} H_2O \\ HNO_3 \end{matrix}\right.$$

from the photolysis of α-dicarbonyls such as methylglyoxal and biacetyl [which are formed during the NO_x-air photooxidations of toluene, the xylenes and the trimethylbenzenes (Atkinson, 1990)],

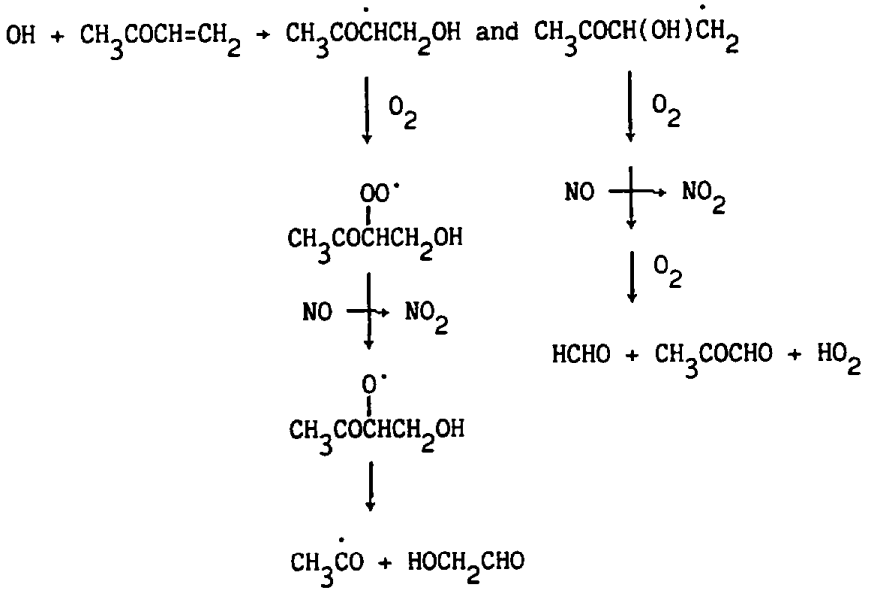
$$CH_3COCHO + h\nu \rightarrow CH_3\dot{C}O + HCO$$

$$CH_3COCOCH_3 + h\nu \rightarrow 2\ CH_3\dot{C}O$$

and from the decomposition reactions of certain β-carboxyalkoxy radicals of the structure $CH_3COC(O^{\cdot})R_1R_2$. These $CH_3COC(O^{\cdot})R_1R_2$ radicals are formed subsequent to OH radical reaction with 2-ketones and certain α,β-unsaturated ketones; for example



(which also forms acetaldehyde)



Thus, acetaldehyde photooxidation is not the only route to PAN formation, although it is expected from the ambient air data of Grosjean (1982) and Grosjean et al. (1983) that the major precursors to PAN formation will be acetaldehyde and the methyl-substituted benzenes.

E. Atmospheric Formation of Acetaldehyde

Acetaldehyde is formed in the troposphere from the tropospheric degradation reactions of many organic compounds. In the "clean" troposphere, CH_3CHO is formed as a product of the atmospheric reactions of ethane

$$OH + C_2H_6 \rightarrow H_2O + C_2H_5^{\cdot}$$

$$C_2H_5^{\cdot} \rightarrow \rightarrow CH_3CH_2O^{\cdot}$$

[involving rapid formation of $CH_3CH_2O_2^{\cdot}$, followed by reactions of the ethyl peroxy radical with NO, NO_2, HO_2 radicals and other organic peroxy radicals to ultimately lead to the formation of the ethoxy ($CH_3CH_2O^{\cdot}$) radical (Atkinson, 1990)], followed by the reaction

$$CH_3CH_2O^{\cdot} + O_2 \rightarrow CH_3CHO + HO_2$$

The steady state concentration of acetaldehyde is then approximately given by

$$[CH_3CHO] \simeq \frac{k_{OH + C_2H_6}}{k_{OH + CH_3CHO}} [C_2H_6]$$

and for a northern hemisphere ethane mixing ratio of ~1 ppb (Blake and Rowland, 1986; Singh et al., 1988) the acetaldehyde mixing ratio will be ~0.02 ppb.

The formation of $CH_3CH_2O^{\cdot}$ and/or $C_2H_5^{\cdot}$ radicals during the atmospheric degradation reactions of organic compounds thus lead to the formation of CH_3CHO. Sources of $C_2H_5^{\cdot}$ radicals include the reaction of propionaldehyde with the OH radical

$$OH + CH_3CH_2CHO \rightarrow H_2O + CH_3\dot{C}HCO$$

$$\downarrow O_2$$

$$CH_3CH_2C(O)OO\cdot$$

$$NO \rightleftarrows NO_2$$

$$C_2H_5\cdot + CO_2$$

and the decomposition reactions of the more complex alkoxy radicals; for example, of the 2-butoxy radical formed from the OH radical-initiated reaction with n-butane

$$CH_3\overset{O\cdot}{C}HCH_2CH_3 \rightarrow CH_3CHO + C_2H_5\cdot$$

This and analogous alkoxy radical decompositions lead directly to CH_3CHO. The β-hydroxyalkoxy radicals formed subsequent to OH radical addition to propene and certain 2-alkenes decompose to form CH_3CHO or the α-hydroxy radical $CH_3\dot{C}HOH$ (Atkinson and Lloyd, 1984; Atkinson, 1990).

$$CH_3\overset{O\cdot}{C}HCH_2OH \rightarrow CH_3CHO + \dot{C}H_2OH$$

$$CH_3CHOHCH_2O\cdot \rightarrow CH_3\dot{C}HOH + HCHO$$

The α-hydroxy radical $CH_3\dot{C}HOH$ forms acetaldehyde by reaction with O_2 (Atkinson and Lloyd, 1984; Atkinson, 1990)

$$CH_3\dot{C}HOH + O_2 \rightarrow CH_3CHO + HO_2$$

In addition, the gas-phase reactions of O_3 with propene and certain 2-alkenes leads to the formation of CH_3CHO. For example, the reaction of O_3 with propene at room temperature and atmospheric pressure is expected to lead to the products (Atkinson, 1990):

$$O_3 + CH_3CH{=}CH_2 \rightarrow 0.50\ CH_3CHO + 0.50\ HCHO + 0.185\ \dot{C}H_2O\dot{O} + 0.09\ \dot{C}H_3CHO\dot{O} + 0.25\ HO_2 + 0.15\ OH + 0.03\ CH_3\dot{O} + 0.31\ CH_3O_2^{\cdot} + 0.07\ CH_4 + 0.065\ H_2 + 0.0325\ CO_2 + 0.40\ CO + 0.22\ H_2O$$

Thus, the atmospheric formation of CH_3CHO from organic precursors occurs in polluted areas characteristic of urban areas, and in many cases this atmospheric formation of CH_3CHO dominates over direct emission of CH_3CHO from combustion sources (Grosjean et al., 1983).

F. Ambient Atmospheric Concentrations of CH_3CHO

The CH_3CHO mixing ratio in the clean lower troposphere is expected to be low, and using a C_2H_6 mixing ratio of ~1 ppb the CH_3CHO mixing ratio is estimated to be ≃0.02 ppb (see Section E above). Reported data for the ambient concentrations of CH_3CHO in California since 1980 are given in Table 4. These data were all collected in the Los Angeles air basin, and vary from ~0.1 ppb up to ~50 ppb, with the most recent concentrations measured in the California Air Resources Board-funded intercomparison study at Claremont in the Los Angeles air basin being significantly lower at <10 ppb. Further, as yet unpublished, ambient CH_3CHO data are available from the 1987 ARB-funded South Coast Air Quality Study (SCAQS).

It may be expected that the ambient atmospheric CH_3CHO levels encountered in the Los Angeles air basin are among the highest to be encountered in California, and hence the ambient atmospheric CH_3CHO mixing ratios in California range from <0.1 ppb (for clean tropospheric air) up to a few tens of ppb, with the actual values depending on the organic precursor emissions, the extent of photochemical activity and the meteorological conditions pertaining.

Table 4. Recent Measurements of Acetaldehyde Concentrations in Ambient Air in California

CH_3CHO Mixing Ratio (ppb)	Measurement Date and Place	Reference
0-32	5-6/1980, Los Angeles	Grosjean (1982)
3-35	9-10/1980, Claremont	Grosjean (1982)
13-38	7-10/1980, Los Angeles	Grosjean et al. (1983)
8-16	7-8/1980, Burbank	Grosjean et al. (1983)
13	7/1980, Pasadena	Grosjean et al. (1983)
3	8/1980, Pacoima	Grosjean et al. (1983)
8	8/1980, Newhall	Grosjean et al. (1983)
16-41	9-10/1980, Rosemead	Grosjean et al. (1983)
56	9/1980, Covina	Grosjean et al. (1983)
38	9/1980, Cucamonga	Grosjean et al. (1983)
25-34	10/1980, El Monte	Grosjean et al. (1983)
15	10/1980, San Dimas	Grosjean et al. (1983)
19	10/1980, Upland	Grosjean et al. (1983)
1.5-10	10/1980, Azusa	Grosjean et al. (1983)
0.1-2.7	10/1980, Lennox	Grosjean et al. (1983)
2-39	9-11/1981, Los Angeles	Grosjean and Fung (1984)
1.0-9.0	9/1985, Claremont	Grosjean (1988)

G. Conclusions

Acetaldehyde is both directly emitted into the atmosphere as well as being formed in the atmosphere from the photochemical degradation of non-methane organic compounds. CH_3CHO is removed from the lower troposphere by reaction with the OH radical and, to a lesser extent, by photolysis, with wet deposition (leading to incorporation of acetaldehyde into rain, cloud and fog water) being expected to be of minor importance. The estimated lifetime of CH_3CHO due to OH radical reaction is ~1 day with this OH radical reaction leading to the formation of (together with other products) peroxyacetyl nitrate (PAN). Reported ambient atmospheric HCHO concentrations in the Los Angeles air basin (expected to have among the higher levels encountered in California) range up ~50 ppb.

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APPENDIX G

ATMOSPHERIC LIFETIME AND FATE OF STYRENE

A Report Submitted in Partial Fulfillment of
California Air Resources Board Contract No. A732-107

"Lifetimes and Fates of Toxic Air Contaminants in
California's Atmosphere"

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TABLE OF CONTENTS

Page

A. Introduction.....G-3

B. Chemical Loss Processes.....G-5

1. Reaction with Ozone.....G-5

2. Reaction with the OH Radical.....G-7

3. Reaction with the NO_3 Radical.....G-9

4. Photolysis.....G-11

C. Physical Loss Processes.....G-11

D. Tropospheric Lifetime and Fate of Styrene.....G-11

E. Atmospheric Formation of Styrene.....G-12

F. Ambient Concentrations of Styrene.....G-12

G. Conclusions.....G-13

H. References.....G-13

A. Introduction

The atmospheric fates of chemical compounds emitted into the troposphere are governed by a number of chemical and physical removal processes. As the result of laboratory studies carried out over the past 20 years, the potentially important gas-phase chemical reaction pathways which must be considered includes:

- Photolysis during daylight hours.
- Reaction with the hydroxyl (OH) radical during daylight hours.
- Reaction with the hydroperoxyl (HO_2) radical, mainly during afternoon/evening hours.
- Reaction with the nitrate (NO_3) radical during nighttime hours.
- Reaction with nitrogen dioxide (NO_2).
- Reaction with ozone (O_3).
- Reaction with gaseous nitric acid (HNO_3).

For the great majority of organic compounds, the most important of these remain photolysis and reaction with hydroxyl (OH) and nitrate (NO_3) radicals and with ozone (O_3).

However, for a limited number of organic compounds, one or more of the other reactive chemical species in the troposphere may react with organic compounds at significant rates. For example, HO_2 radicals react with formaldehyde and, more slowly, with acetaldehyde and glyoxal; NO_2 reacts with dialkenes; and gaseous HNO_3 reacts with basic compounds such as the amines.

Additionally, for chemical compounds present in the adsorbed phase, photolysis and reaction with O_3, N_2O_5, NO_2, HNO_3, HONO, H_2SO_4 and hydrogen peroxide (H_2O_2) may contribute to their degradation. For certain of these reactions involving adsorbed organics, synergistic interactions may be of importance.

The physical removal processes can be defined in a simplistic manner as accretion (or coagulation) of particles, and dry and wet deposition of gases and particles. Removal of gases and particles at ground surfaces (including snow and other moist surfaces) is referred to as dry deposition, while removal of these species by precipitation is referred to as wet deposition. Our current understanding of these processes, which are

dynamic in nature, must be considered to be semi-quantitative at the present time, and in general there is a lack of experimental data concerning these processes for most organic compounds (Atkinson, 1988; Bidleman, 1988).

The atmospheric lifetime τ of a chemical is defined as the time to decay to a concentration of 1/e (=0.368) of that initially present. Also,

$$\frac{1}{\tau} = \frac{1}{\tau_{\text{chemical}}} + \frac{1}{\tau_{\text{physical}}} \qquad (1)$$

where $\tau_{chemical}$ and $\tau_{physical}$ are the lifetimes of the chemical with respect to only chemical reaction and only physical loss processes, respectively. These chemical and physical lifetimes are composites of those for the individual loss processes, for example

$$\frac{1}{\tau_{\text{chemical}}} = \frac{1}{\tau_{\text{photolysis}}} + \frac{1}{\tau_{OH}} + \frac{1}{\tau_{NO_3}} + \frac{1}{\tau_{O_3}} \ldots \qquad (2)$$

where $\tau_{photolysis}$, τ_{OH}, τ_{NO_3} and τ_{O_3} are the lifetimes with respect to photolysis, reaction with the OH radical, reaction with the NO_3 radical, and reaction with O_3, respectively. In turn, these reactive loss processes are determined by the rate constants, k_x, for reaction and the ambient atmospheric concentrations, [X], of the reactive intermediates. For example

$$\frac{1}{\tau_{OH}} = k_{OH}[OH]$$

For photolysis, the photolysis rate depends on the absorption cross section (σ), the photolysis quantum yield (ϕ), and the radiation intensity (J), all of which are wavelength dependent:

$$\frac{1}{\tau_{photolysis}} = k_{photolysis} = \int_{\sim 290\ nm}^{\sim 800\ nm} \sigma_\lambda \phi_\lambda J_\lambda \, d\lambda$$

In this report, the available literature data concerning the chemical and physical removal processes for styrene ($C_6H_5CH=CH_2$) are presented and its resulting atmospheric lifetime is estimated. The atmospheric chemistry of this compound is also discussed. Styrene is gaseous at room temperature, and hence this report focusses on the potential gas-phase atmospheric loss processes.

B. Chemical Loss Processes

1. Reaction with Ozone

The rate constants determined for the gas-phase reaction of O_3 with styrene are given in Table 1. All three rate constant determinations have been carried out at room temperature, and the measured rate constants are in reasonable agreement. In particular, the two most recent absolute rate constant determinations of Atkinson et al. (1982, 1989) are in good agreement, and a weighted average of these two rate constants leads to the recommended rate constant of

$$k_1 = 1.8 \times 10^{-17}\ cm^3\ molecule^{-1}\ s^{-1}$$

at 298 K, with an estimated overall uncertainty of ±40%.

The magnitude of this rate constant, when compared to the literature rate constants at room temperature for the gas-phase reactions of O_3 with benzene and the methyl-substituted benzenes of $k < 10^{-20}\ cm^3\ molecule^{-1}\ s^{-1}$ (Atkinson and Carter, 1984), shows that the reaction of O_3 with styrene proceeds by initial addition of O_3 to the $-CH=CH_2$ substituent group. Product studies using *in situ* long pathlength Fourier transform infrared (FT-IR) absorption spectroscopy to monitor the reactants and products (Atkinson et al., 1989) showed that the major products of the gas-phase reaction of O_3 with styrene in one atmosphere of air were formaldehyde (HCHO) and benzaldehyde (C_6H_5CHO), together with a minor amount of formic acid (HCOOH). The observed product yields were: HCHO and C_6H_5CHO, each ~40%; and HCOOH, ~1-2%. Analyses of reaction samples from analogous experiments by gas chromatography (GC) and combined gas chromatography-

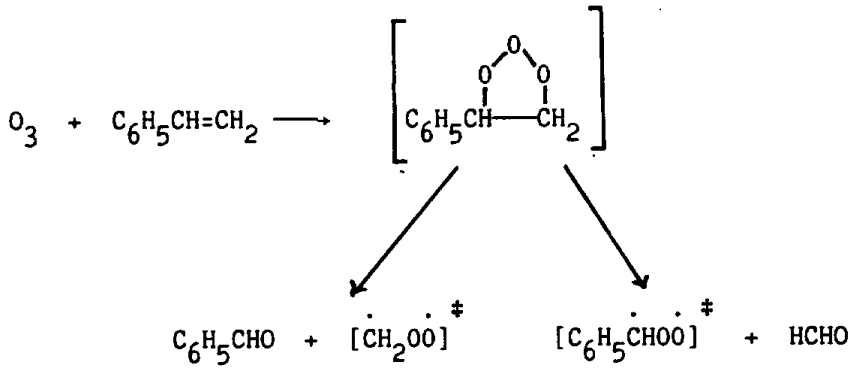
Table 1. Rate Constants, k_1 for the Gas-Phase Reaction of O_3 with Styrene

$10^{17} \times k_1$ (cm^3 $molecule^{-1}$ s^{-1})	at T (K)	Technique[a]	Reference
3.0	303	F-CA	Bufalini and Altshuller (1965)
2.16 ± 0.46	296 ± 2	S-CL	Atkinson et al. (1982)
1.71 ± 0.18	296 ± 2	S-CL	Atkinson et al. (1989)

[a]Symbols: F, flow system; S, static system; CA, chemical analysis by wet chemical methods; CL, ozone monitored by chemiluminescence.

mass spectrometry (GC-MS) yielded the same major products as identified from the FT-IR data.

The available kinetic and product data suggest that the reaction then proceeds by



where [ ]‡ denotes an initially energy-rich biradical species. The subsequent reactions of the $[\dot{C}H_2O\dot{O}]^{\ddagger}$ radical formed from the O_3 + ethene reaction have been discussed in detail previously (Atkinson and Lloyd, 1984; Atkinson and Carter, 1984; Atkinson, 1990). At atmospheric pressure of air and room temperature

$$[\dot{C}H_2O\dot{O}] \xrightarrow{M} \dot{C}H_2O\dot{O} \qquad (37\%)$$

$$\longrightarrow CO_2 + H_2 \qquad (\sim 13\%)$$

$$\longrightarrow CO + H_2O \qquad (\sim 44\%)$$

$$\longrightarrow 2H + CO_2 \qquad (\sim 6\%)$$

with the thermalized $\dot{C}H_2O\dot{O}$ biradical being expected to react with water vapor to form HCOOH under atmospheric conditions. The reactions of the $[C_6H_5\dot{C}HO\dot{O}]^{\ddagger}$ radical are not presently known. The product data obtained by Atkinson et al. (1989) are reasonably consistent with the above reaction scheme, providing that the $[C_6H_5\dot{C}HO\dot{O}]^{\ddagger}$ biradical does not produce C_6H_5CHO in high yield.

2. Reaction with the OH Radical

Rate constants for the gas-phase reactions of the OH radical with styrene have been determined at room temperature by Bignozzi et al. (1981) and Atkinson and Aschmann (1988) using relative rate techniques. The rate constants from these two studies, as reevaluated by Atkinson (1989) to be consistent with the most recent data for the rate constants for the reference reactions, are given in Table 2. The agreement is excellent, and a rate constant of

$$k_2 = 5.8 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

was recommended by Atkinson (1989). Analogous to the O_3 reaction, the magnitude of the rate constant k_2 suggests that the reaction of the OH radical with styrene proceeds by initial OH radical addition to the substituent $-CH=CH_2$ group

$$OH + C_6H_5CH=CH_2 \rightarrow C_6H_5\dot{C}HCH_2OH \text{ and } C_6H_5CHOH\dot{C}H_2$$

The products of the OH radical reaction with styrene in air have been investigated by Bignozzi et al. (1981) and Atkinson et al. (1989). Bignozzi et al. (1981) observed benzaldehyde as the major product, and derived a formation yield of benzaldehyde of 1.03 ± 0.15 from the time-concentration profiles of styrene and benzaldehyde in an irradiated NO_x - styrene - air mixture. More recently, Atkinson et al. (1989) have used long pathlength FT-IR absorption spectroscopy to monitor the reactants and

Table 2. Literature Rate Constants k_2 for the Gas-Phase Reaction of the OH Radical with Styrene

$10^{11} \times k_2$ (cm^3 $molecule^{-1}$ s^{-1})	at T (K)	Technique[a]	Reference
52 ± 5	298 ± 2	RR [relative to k(OH + 2,2,4-trimethylpentane) = 3.68×10^{-12}][b]	Bignozzi et al. (1981)
58.1 ± 1.5	296 ± 2	RR [relative to k(OH + 2-methyl-1,3-butadiene) = 1.01×10^{-10}][b]	Atkinson and Aschmann (1988)

[a]Symbols: RR, relative rate.
[b]Recommendations of Atkinson (1989).

products in irradiated C_2H_5ONO - NO - styrene - air mixtures, and observed HCHO and C_6H_5CHO as the major products, with formation yields of 0.90 and ~0.75, respectively. A further product was observed by Atkinson et al. (1989) which contained a nitrate ($-ONO_2$) group. Heuss and Glasson (1968) also observed HCHO and C_6H_5CHO as the major products of the NO_x - air photooxidation of styrene.

The products observed in these studies are those expected to arise from the reactions subsequent to the initial OH radical addition to the $-CH=CH_2$ substituent group. Thus, in the presence of NO, and neglecting the formation of organic nitrates from the reaction of the peroxy radicals with NO,

$$C_6H_5\dot{C}HCH_2OH + O_2 \xrightarrow{M} C_6H_5CH(OO\cdot)CH_2OH$$

$$C_6H_5CH(OO\cdot)CH_2OH + NO \rightarrow C_6H_5CH(O\cdot)CH_2OH + NO_2$$

$$C_6H_5\overset{O\cdot}{\underset{|}{C}}HCH_2OH \rightarrow C_6H_5CHO + \dot{C}H_2OH$$

$$\dot{C}H_2OH + O_2 \rightarrow HCHO + HO_2$$

and

$$C_6H_5\dot{C}HOHCH_2 + O_2 \xrightarrow{M} C_6H_5CHOHCH_2OO\cdot$$

$$C_6H_5CHOHCH_2OO\cdot + NO \rightarrow C_6H_5CHOHCH_2O\cdot + NO_2$$

$$C_6H_5CHOHCH_2O\cdot \rightarrow C_6H_5\dot{C}HOH + HCHO$$

$$C_6H_5\dot{C}HOH + O_2 \rightarrow C_6H_5CHO + HO_2$$

3. Reaction with the NO_3 Radical

To date there has only been one determination of the rate constant for the gas-phase reaction of the NO_3 radical with styrene. Using a relative rate technique, Atkinson and Aschmann (1988) determined the rate constant k_3 relative to the rate constant for trans-2-butene at 296 ± 2 K and, using a rate constant for the reaction of the NO_3 radical with trans-2-butene of (3.87 ± 0.45) x 10^{-13} cm^3 $molecule^{-1}$ s^{-1} (Ravishankara and Mauldin, 1985; Dlugokencky and Howard, 1989), this leads to

$$k_3 = (1.51 \pm 0.18) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

at 296 ± 2 K.

The products of the gas-phase reaction of styrene with the NO_3 radical have been investigated by Atkinson et al. (1989) using long path-length FT-IR absorption spectroscopy to monitor the reactants and products. Formaldehyde (HCHO) and benzaldehyde (C_6H_5CHO) were observed as products, with equal formation yields of ~0.10-0.12.

Three as yet unidentified nitrogen-containing compounds were the most conspicuous products of these NO_3 radical reactions with styrene (Atkinson et al., 1989). These products (A, B and C) had infrared absorption bands which indicated the presence of the following groups: A, $-ONO_2$ and $-OONO_2$; B and C, $-ONO_2$ and >C=O. Product A was formed in the initial stages of the reaction, and then disappeared rapidly (as expected from the presence of the thermally unstable peroxynitrate, $-OONO_2$, group). Product B was more stable than A, but a steady decrease in its concentration with time was also observed (Atkinson et al., 1989). Product C was the most stable of these three nitrogen-containing compounds.

The NO_3 radical reaction with styrene is expected to proceed by initial NO_3 radical addition to the $-CH=CH_2$ substituent group:

$$NO_3 + C_6H_5CH=CH_2 \rightarrow C_6H_5CH(ONO_2)\dot{C}H_2 \text{ and } C_6H_5\dot{C}HCH_2ONO_2$$

followed by the reactions (taking the $C_6H_5\dot{C}HCH_2ONO_2$ radical as an example)

$$C_6H_5\dot{C}HCH_2ONO_2 + O_2 \rightarrow C_6H_5\underset{\displaystyle OO\cdot}{C}HCH_2ONO_2$$

$$C_6H_5\underset{\displaystyle OO\cdot}{C}HCH_2ONO_2 + NO \rightleftarrows C_6H_5\underset{\displaystyle OONO_2}{C}HCH_2ONO_2$$

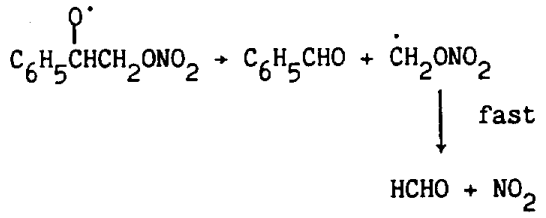
(possibly product A)

$$C_6H_5\underset{\displaystyle OO\cdot}{C}HCH_2ONO_2 + \begin{cases} NO \\ RO_2\cdot \end{cases} \rightarrow C_6H_5\underset{\displaystyle O\cdot}{C}HCH_2ONO_2$$

(where the $RO_2\cdot$ radical can include the $C_6H_5\underset{\displaystyle OO\cdot}{C}HCH_2ONO_2$ or $C_6H_5CH(ONO_2)CH_2OO\cdot$ radical)

$$C_6H_5\underset{\displaystyle O\cdot}{C}HCH_2ONO_2 + O_2 \rightarrow C_6H_5COCH_2ONO_2 + HO_2$$

(possibly product C)



Analogous intermediate or first-generation products ($C_6H_5CH(ONO_2)CH_2OONO_2$ and $C_6H_5CH(ONO_2)CHO$) are expected to be formed from the $C_6H_5CH(ONO_2)\dot{C}H_2$ radical.

4. Photolysis

According to Calvert and Pitts (1966), in solution styrene has its largest wavelength absorption cross-section of ~2 x 10^{-20} cm^2. There is no evidence for photolysis of styrene being of importance in the studies of Bignozzi et al. (1981) or Atkinson and Aschmann (1988). In particular, the good agreement between the studies of Bignozzi et al. (1981) and Atkinson and Aschmann (1988) concerning the OH radical reaction rate constant indicates that photolysis was of minor or negligible significance in the NO_x-styrene-air irradiations carried out by Bignozzi et al. (1981), in which the light intensity and spectral distribution and OH radical concentration approximated those in ambient air.

C. Physical Loss Processes

No data are available for styrene concerning dry and/or wet deposition. Since styrene is a hydrocarbon present in the gas phase, it is expected that dry and wet deposition will be of negligible importance as tropospheric loss processes for styrene, especially when compared to the relatively short tropospheric lifetime calculated from the gas-phase chemical loss process (see Section D below).

D. Tropospheric Lifetime and Fate of Styrene

As discussed in Section A, the tropospheric lifetime of styrene is determined from the loss rates of both the chemical and physical loss processes. The physical loss processes are expected to be of no significance, and the tropospheric lifetime of styrene is determined by its reactions with OH and NO_3 radicals and O_3. Using measured or estimated tropospheric concentrations of these species of: OH radicals, 1.5 x 10^6

molecule cm^{-3} during daylight hours (Prinn et al., 1987); NO_3 radicals, 2.4 x 10^8 molecule cm^{-3} during nighttime hours (Platt et al., 1984; Atkinson et al., 1986); and O_3, 7 x 10^{11} molecule cm^{-3} throughout a 24-hr period (Logan, 1985), the tropospheric loss rates of styrene due to these chemical reactions can be assessed. The calculated lifetimes for these individual reactions are then: reaction with the OH radical, 3.2 hrs; reaction with the NO_3 radical, 7.7 hrs; and reaction with O_3, 22 hr. The daytime OH radical reaction is the dominant of the reaction loss processes, leading to a tropospheric lifetime of styrene during daylight hours of ~3 hrs.

As discussed in Section B.2 above, the tropospheric degradation of styrene will then lead (by reaction with the OH radical) to the formation of HCHO and C_6H_5CHO in high yield, and the tropospheric degradation of styrene will lead to the formation in the atmosphere of both formaldehyde and benzaldehyde. It should also be noted that the tropospheric degradation of benzaldehyde will lead to the production in the atmosphere of peroxybenzoyl nitrate [PBzN; $C_6H_5C(O)OONO_2$] (Atkinson and Lloyd, 1984; Atkinson, 1990).

E. Atmospheric Formation of Styrene

As presently understood, there are no in situ atmospheric formation processes leading to styrene from other organics emitted into the troposphere from anthropogenic or biogenic sources.

F. Ambient Concentrations of Styrene

Styrene has not been identified in most ambient atmospheric monitoring studies nor in emission studies. However, Grosjean and Fung (1984) report the presence of styrene in 16 ambient air samples collected in downtown Los Angeles in the fall of 1981, with the styrene mixing ratios being in the range 0.5-3 part-per-billion (ppb). Ambient air samples collected in August 1986 in Glendora during the Carbonaceous Species Measurement Comparison Study did not show the presence of styrene (D. Lawson, California Air Resources Board; private communication, 1989).

G. Conclusions

Styrene is removed from the troposphere by chemical reaction with OH and NO_3 radicals and O_3, with the daytime OH radical reaction being expected to dominate and to lead to a styrene lifetime of ~3 hrs during daylight hours. The photooxidation of styrene leads to the production in the atmosphere of formaldehyde (HCHO) and benzaldehyde (C_6H_5CHO) in close to unit yield.

Styrene is not formed in the atmosphere from either anthropogenic or biogenic emissions, and ambient air measurement data show that the styrene mixing ratios in the Los Angeles air basin are a few ppb or less.

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APPENDIX H

ATMOSPHERIC LIFETIME AND FATE OF DIESEL EXHAUST PARTICLES AND GAS- AND PARTICLE-PHASE PAH AND PAH-DERIVATIVES

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"Lifetimes and Fates of Toxic Air Contaminants in California's Atmosphere"

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TABLE OF CONTENTS

Page

A. Introduction....H-3

B. Physical and Chemical Characterization of Diesel Particles and PAH and PAH-Derivatives....H-6

1. Particle-Size Distribution....H-6
2. PAH and PAH-Derivatives....H-6
3. Nitro-PAH....H-12

C. Physical Loss Processes....H-13

D. Gas-Phase Loss Processes of PAH and PAH-Derivatives....H-14

1. Wet Deposition of Gas-Phase PAH and PAH-Derivatives....H-14
2. Reaction with the OH Radical....H-16
3. NO_3 Radical Reactions....H-30
4. O_3 Reactions....H-37
5. Photolysis....H-37
6. Atmospheric Lifetimes of Gas-Phase PAH and PAH-Derivatives....H-37
7. Evidence for Atmospheric Transformations of PAH....H-41

E. Adsorbed-Phase Loss Processes of PAH and PAH-Derivatives....H-44

1. Reaction with O_3....H-45
2. Reaction with Oxides of Nitrogen....H-47
3. Photolysis....H-49
4. Ambient Air Data....H-50

F. Atmospheric Formation Processes....H-51

G. References....H-52

A. Introduction

The atmospheric fates of chemical compounds emitted into the troposphere are governed by a number of chemical and physical removal processes. As the result of laboratory studies carried out over the past 20 years, it is recognized that the potentially important gas-phase chemical reaction pathways include:

- Photolysis during daylight hours
- Reaction with the hydroxyl (OH) radical during daylight hours
- Reaction with the hydroperoxyl (HO_2) radical, mainly during afternoon/evening hours
- Reaction with the nitrate (NO_3) radical during nighttime hours
- Reaction with nitrogen dioxide (NO_2)
- Reaction with ozone (O_3)
- Reaction with gaseous nitric acid (HNO_3)

For the great majority of organic compounds which are present in the gas phase, the most important of these loss processes are photolysis and reaction with hydroxyl (OH) and nitrate (NO_3) radicals and ozone (O_3).

However, for a limited number of gaseous organic compounds, one or more of the other reactive chemical species in the troposphere may react with these organic compounds at significant rates. For example, HO_2 radicals react with formaldehyde and, more slowly, with acetaldehyde and glyoxal; NO_2 reacts with conjugated dienes; and gaseous HNO_3 reacts with basic compounds such as the amines.

For chemical compounds present in the adsorbed phase, photolysis and reaction with O_3, N_2O_5, NO_2, HNO_3, HONO, H_2SO_4 and hydrogen peroxide (H_2O_2) may contribute to their degradation. For certain of these reactions involving adsorbed organics, synergistic interactions may be of importance.

The physical removal processes can be defined in a simplistic manner as accretion (or coagulation) of particles, and dry and wet deposition of gases and particles. Removal of gases and particles at ground surfaces (including snow and other moist surfaces) is referred to as dry deposition, while removal of these species by precipitation is referred to as wet deposition. Our understanding of these processes, which are dynamic

in nature, must be considered to be semi-quantitative at the present time, and in general there is a lack of experimental data concerning these processes for most organic compounds (Atkinson, 1988; Bidleman, 1988).

The atmospheric lifetime τ of a chemical is defined as the time to decay to a concentration of 1/e (=0.368) of that initially present. Also,

$$\frac{1}{\tau} = \frac{1}{\tau_{chemical}} + \frac{1}{\tau_{physical}} \qquad (1)$$

where $\tau_{chemical}$ and $\tau_{physical}$ are the lifetimes of the chemical with respect to only chemical reaction and only physical loss processes, respectively. These chemical and physical lifetimes are composites of those for the individual loss processes, for example

$$\frac{1}{\tau_{chemical}} = \frac{1}{\tau_{photolysis}} + \frac{1}{\tau_{OH}} + \frac{1}{\tau_{NO_3}} + \frac{1}{\tau_{O_3}} \ldots \qquad (2)$$

where $\tau_{photolysis}$, τ_{OH}, τ_{NO_3} and τ_{O_3} are the lifetimes with respect to photolysis, reaction with the OH radical, reaction with the NO_3 radical, and reaction with O_3, respectively. In turn, these reactive loss processes are determined by the rate constants, k_x, for reaction and the ambient atmospheric concentrations, [X], of the reactive intermediates. For example

$$\frac{1}{\tau_{OH}} = k_{OH}[OH]$$

For photolysis, the photolysis rate depends on the absorption cross section (σ), the photolysis quantum yield (ϕ), and the radiation intensity (J), all of which are wavelength dependent:

$$\frac{1}{\tau_{photolysis}} = k_{photolysis} = \int_{\sim 290\ nm}^{\sim 800\ nm} \sigma_\lambda \phi_\lambda J_\lambda \, d\lambda$$

In this report, we describe the available literature data concerning the physical and chemical removal processes for the particulate matter and the gas- and particle-phase polycyclic aromatic hydrocarbons (PAH) and PAH-derivatives emitted in diesel exhaust. In addition to particles and gas- and particle-phase PAH and PAH-derivatives, the exhaust from diesel-fueled vehicles is comprised of a wide spectrum of inorganic and organic compounds, including carbon dioxide (CO_2), carbon monoxide (CO), water vapor (H_2O), oxides of nitrogen (NO_x, consisting mainly of NO + NO_2), formaldehyde (HCHO) and other saturated and unsaturated aldehydes and ketones, alkanes, alkenes and monocyclic aromatic hydrocarbons (see, for example, National Research Council, 1983; Jonsson et al., 1985; Hayano et al., 1985; Schuetzle and Frazier, 1986; Obuchi et al., 1987; Johnston, 1988). Discussion of the lifetimes and fates of all of these emitted species is beyond the scope of this document, which focuses on the following:

- The tropospheric lifetime and fate of particle matter emitted from diesel-fueled vehicles.

- The atmospheric lifetimes and fates of PAH and PAH-derivatives which are present in the atmosphere at least partially in the gas phase.

- The atmospheric lifetimes and fates of PAH and PAH-derivatives which are particle-associated in the atmosphere.

The processes to be considered are then

- Physical loss processes for the particles on which, or in which, the PAH and PAH-derivatives reside.

- The gas-phase tropospheric removal and/or transformation processes for PAH and PAH-derivatives present in the gas-phase.

- Adsorbed-phase reactions of PAH and PAH-derivatives.

B. Physical and Chemical Characterization of Diesel Particles and PAH and PAH-Derivatives

1. Particle-Size Distribution

The particles emitted from diesel-fueled vehicles have mass-median aerodynamic diameters in the range 0.1-0.25 μm (Groblicki and Begeman, 1979; Dolan et al., 1980; National Research Council, 1982; Williams, 1982; Pierson et al., 1983), with more than 75% of the mass being associated with particles of diameter <1 μm (Pierson et al., 1983). The composition of diesel exhaust particulate is mainly elemental carbon, which is then a good carrier for organic compounds of low volatility which can reside on the particle surface or be included inside the particles. The position of attachment of organic compounds on or in the particles can profoundly affect the atmospheric chemistry and lifetimes of these compounds, since those organic compounds present inside the largely elemental carbon particles are prevented from volatilizing into the gas phase and are protected against photolysis and chemical reaction, while those organic compounds present on the surface of the particles can undergo volatilization into the gas phase and be susceptible to photolysis and/or chemical reaction. As noted by the National Research Council (1983), diesel exhaust particulate is typically 25% extractable into organic solvents, although there is a wide variability in the percent extractable, from 10-90%, depending on the vehicle and operating conditions (see, for example, Williams et al., 1989).

2. PAH and PAH-Derivatives

A chemical analysis of the non-polar and moderately polar fractions of a diesel exhaust sample collected on filters from an exhaust dilution tube is given in Table 1 [adapted from Schuetzle (1983)]. A large proportion of diesel particulate extracts are heavy aliphatic hydrocarbons and it seems generally accepted that these are mainly unburnt fuel or lubricant oil components (Obuchi et al., 1987; Barbella et al.,

Table 1. Analysis of Nonpolar and Moderately Polar Fractions of an Extract of Diesel Particles Collected on Filters using an Exhaust Dilution Tube (from Schuetzle, 1983)

Compound	Approximate Concentration in Oldsmobile Extract (ppm)
Nonpolar fractions	
Phenanthrenes and anthracene	600
Methylphenanthrenes and methylanthracenes	1,400
Dimethylphenanthrenes and dimethylanthracenes	3,200
Pyrene	1,700
Fluoranthene	1,400
Methylpyrenes and methylfluoranthenes	800
Chrysene	100
Cyclopenta[cd]pyrene	20
Benzo[ghi]fluoranthene	100
Benz[a]anthracene	500
Benzo[a]pyrene	40
Other PAHs, heterocyclics	34,000
HCs and alkylbenzenes	510,000
Total nonpolar fractions	556,000
Moderately polar fractions	
PAH ketones	
Fluorenones	4,000
Methylfluorenones	400
Dimethylfluorenones	200
Anthrones and phenanthrones	1,600
Methylanthrones and methylphenanthrones	1,600
Dimethylanthrones and dimethylphenanthrones	1,300
Fluoranthones and pyrones	1,200
Benzanthrones	200
Xanthones	300
Methylxanthones	200
Thioxanthones	1,600
Methylthioxanthones	900
Total	13,500
PAH carboxaldehydes	
Fluorene carboxaldehydes	1,600
Methyl fluorene carboxaldehydes	400
Phenanthrene and anthracene carboxaldehydes	2,600
Methylanthracene and methylphenanthrene carboxaldehydes	1,600
Dimethylanthracene and dimethylphenanthrene carboxaldehydes	400
Benz[a]anthracene, chrysene, and triphenylene carboxaldehydes	400
Naphthalene dicarboxaldehydes	300
Dimethylnaphthalene carboxaldehydes	300
Trimethylnaphthalene carboxaldehydes	1,000
Pyrene and fluoranthene carboxaldehydes	1,600

Table 1 (continued) - 2

Compound	Approximate Concentration in Oldsmobile Extract (ppm)
Xanthene carboxaldehydes	600
Dibenzofuran carboxaldehydes	400
Total	11,200
PAH acid anhydrides	
Naphthalene dicarboxylic acid anhydrides	2,900
Methylnaphthalene dicarboxylic acid anhydrides	1,000
Dimethylnaphthalene dicarboxylic acid anhydrides	500
Anthracene and phenanthrene dicarboxylic acid anhydrides	600
Total	5,000
Hydroxy PAHs	
Hydroxyfluorene	1,400
Methylhydroxyfluorene	400
Dimethylhydroxyfluorene	1,500
Hydroxyanthracenes and hydroxyphenanthrenes	600
Hydroxymethylanthracenes and hydroxymethylphenanthrenes	900
Hydroxydimethylanthracenes and hydroxydimethylphenanthrenes	1,300
Hydroxyfluorenone	2,100
Hydroxyxanthone	1,300
Hydroxyxanthene	1,000
Total	10,400
PAH quinones	
Fluorene quinones	700
Methylfluorene quinones	600
Dimethylfluorene quinones	500
Anthracene and phenanthrene quinones	1,900
Methylanthracene and methylphenanthrene quinones	2,100
Fluoranthene and pyrene quinones	200
Naphtho[1,8-cd]pyrene 1,3-dione	600
Total	6,500
Nitro-PAHs	
Nitrofluorenes	30
Nitroanthracenes and nitrophenanthrenes	70
Nitrofluoranthenes	5
Nitropyrenes	150
Methylnitropyrenes and methylnitrofluoranthenes	20
Total	270
Other oxygenated PAHs	7,700
PAH carryover from nonpolar fraction	6,000
Phthalates, HC contaminants	31,000
Total, moderately polar fractions	92,000

1989). In addition to a wide range of PAH, with methylated PAH being the most abundant, over one hundred species were identified in the moderately polar fractions of a diesel exhaust extract (Schuetzle et al., 1981). The moderately polar fractions contain mainly PAH derivatives including hydroxy, ketone, quinone, carboxaldehyde, acid anhydride and nitro derivatives of PAH (Schuetzle et al., 1981).

The PAH present in diesel exhaust may be either unburned fuel components or combustion-formed PAH. Some researchers have found the major PAH emissions to be unburned fuel components such as naphthalene, fluorene, phenanthrene and their alkyl derivatives (Williams et al., 1986), while other researchers have found the light naphthalenes present in the fuel to be absent from the exhaust (Barbella et al., 1989). Certain PAH, when added to a hexadecane fuel, have been found to promote soot formation and the emissions of other PAH, while the addition of pyrene or phenanthrene increased the emission of these PAH, but caused no increased soot formation (Henderson et al., 1984). There is some evidence that benzo[a]pyrene and other PAH may be formed during the combustion process (Henderson et al., 1984; Kittelson et al., 1985; Obuchi et al., 1987; see also below) and, consistent with PAH formation, diesel combustion of fuels containing no PAH still results in PAH emissions (Barbella et al., 1989).

Kittelson et al. (1985) measured selected PAH and 1-nitropyrene concentrations in the cylinder and the exhaust manifold of an operating 5.7-liter V-8 diesel engine and observed that the PAH concentrations were higher in the cylinder than in the exhaust manifold, in contrast to higher 1-nitropyrene concentrations in the exhaust manifold. These data suggest (Kittelson et al., 1985) that the PAH are formed early in the combustion process and subsequently decay in the high temperature environment of the expansion stroke and the exhaust process. In contrast, 1-nitropyrene appears to be formed during the expansion and exhaust processes (Kittelson et al., 1985).

Laboratory investigations of the formation of PAH and soot in flames have shown that PAH are formed from non-PAH containing fuels, and that both PAH formation and destruction occur under combustion conditions (see, for example, Bockhorn et al. 1981; Ciajolo et al., 1982; Prado et al., 1985; Toqan et al., 1985; Frenklach et al., 1988; Frenklach, 1989). These

studies conclude that hydrogen atoms are involved in the formation/destruction reactions of PAH (Bockhorn et al., 1981; Frenklach et al., 1988; Frenklach, 1989) and suggest that the PAH are precursors to soot formation (Bockhorn et al., 1981; Ciajolo et al., 1982; Prado et al., 1985; Toqan et al., 1985; Frenklach et al., 1988; Kroto, 1988; Frenklach, 1989).

As is the case for combustion sources in general, a wide spectrum of PAH and alkyl-PAH are emitted from diesel exhaust (see above and Schuetzle et al., 1981; National Research Council, 1983; Jensen and Hites, 1983; Williams et al., 1986; Barbella et al., 1988, 1989). These PAH exhibit a wide range of volatilities (Table 2) and in the atmosphere are distributed between the gas and particle phases (Coutant et al., 1988; Arey et al., 1987, 1989a; Atkinson et al., 1988). Naphthalene and the other two ring PAH (including biphenyl) are present in ambient air in the gas phase, while the ≥5-ring PAH such as benzo[a]pyrene are particle associated. As discussed by Bidleman and Foremen (1987), Bidleman (1988) and Pankow (1989), the vapor pressure parameter determining the phase distribution of semivolatile organic compounds is the subcooled liquid vapor pressure and not the solid-phase vapor pressure.

Based upon the ambient air sampling measurements of Coutant et al. (1988), those PAH with subcooled liquid vapor pressures of $<10^{-6}$ Torr are essentially totally particle associated, and those with higher subcooled liquid vapor pressures are present, at least partially, in the gas phase. Thus, Bidleman (1988) concludes from ambient air monitoring data that the majority of fluoranthene and pyrene (subcooled liquid vapor pressures ~4 x 10^{-5} Torr) are present in the gas phase, that benz[a]anthracene (subcooled liquid vapor pressure ~2 x 10^{-6} Torr) is approximately equally distributed between gas and particle phase, and that benzo[a]pyrene (subcooled liquid vapor pressure ~9 x 10^{-8} Torr) is essentially totally particle associated. This translates into PAH with ≥5 rings being particle associated, and PAH with ≤4 rings being, at least partially, in the gas phase in ambient air. A similar distribution between gas- and particle-phase will occur for the PAH-derivatives, with, for example, the ≥4-ring nitro-PAH being particle-associated.

Table 2. Literature Room Temperature Vapor Pressures (Torr) for PAH

PAH	Vapor pressure at 298 K (Torr)	
	Solid[a]	Subcooled Liquid[b]
Naphthalene	7.8×10^{-2}	1.3×10^{-1}
Biphenyl	9.9×10^{-3} [c]	2.1×10^{-2}
Acenaphthylene	6.7×10^{-3}	
Acenaphthene	2.2×10^{-3}	7.6×10^{-3}
Fluorene	6.0×10^{-4}	3.1×10^{-3}
Phenanthrene	1.2×10^{-4}	5.3×10^{-4}
Anthracene	6.0×10^{-6}	5.0×10^{-4}
Fluoranthene	9.2×10^{-6}	5.2×10^{-5}
Pyrene	4.5×10^{-6}	3.3×10^{-5}
Benzo[a]fluorene		1.2×10^{-5}
Benzo[b]fluorene		1.1×10^{-5}
Benz[a]anthracene	2.1×10^{-7}	1.9×10^{-6}
Chrysene		1.7×10^{-6}
Triphenylene		1.7×10^{-6}
Benzo[b]fluoranthene		1.6×10^{-7}
Benzo[k]fluoranthene		1.6×10^{-7}
Benzo[e]pyrene		1.0×10^{-7}
Benzo[a]pyrene		9.0×10^{-8}
1-Methylnaphthalene	6.7×10^{-2}	
2-Methylnaphthalene	5.4×10^{-2} [d]	

[a]From Sonnefeld et al. (1983) unless indicated.
[b]From Yamasaki et al. (1984).
[c]From Mackay et al. (1982).
[d]From Macknick and Prausnitz (1979).

3. Nitro-PAH

The presence of nitroarenes in diesel exhaust particulate extracts has received much attention because of the strong mutagenic activity of certain nitro-PAH, and numerous studies of the health effects of nitro-PAH have been conducted over the past ten years (see for example, Rosenkranz and Mermelstein, 1983; Tokiwa and Ohnishi, 1986; King, 1988; and references therein). More than fifty nitro-PAH have been tentatively identified in diesel exhaust, including mononitro-PAH, mononitro-alkyl-PAH, di- and trinitro-PAH and oxygenated nitro-PAH, such as nitrofluorenone (Schuetzle et al., 1982; Xu et al., 1982; Paputa-Peck et al., 1983; Robbat et al., 1986).

When isomer-specific analyses have been conducted, the major nitroarenes observed in diesel exhaust have been the isomers formed by electrophilic nitration of the parent PAH and in amounts consistent with the abundance and reactivity (Schuetzle, 1983; Nielsen, 1984) of the parent PAH toward electrophilic nitration. For example, 1-nitropyrene, 2-nitrofluorene, 9-nitroanthracene (Schuetzle and Perez, 1983; Paputa-Peck et al., 1983; Robbat et al., 1986), 6-nitrobenzo[a]pyrene (Gibson 1982; 1983; Schuetzle and Perez, 1983; Paputa-Peck et al., 1983) and 3-nitrofluoranthene (Robbat et al., 1986) have been observed in diesel exhaust extracts, all nitro-PAH isomers that are the major electrophilic nitration products of the parent PAH (Ruehle et al., 1985). Thus, although the PAH isomer-pair of fluoranthene and pyrene are present in diesel exhaust in very similar amounts (see Table 1), 1-nitropyrene is found in diesel exhaust particles in large excess over 3-nitrofluoranthene (Schuetzle et al., 1982; Paputa-Peck et al., 1983; Robbat et al., 1986).

Adding pyrene to hexadecane fuel in a single cylinder diesel engine increased nitropyrene emissions (Henderson et al., 1984). Henderson et al. (1984) suggested that since the nitropyrene/pyrene ratio decreased with increasing pyrene emissions, the active NO_x species in the exhaust stream could be the limiting factor in nitro-PAH formation. Schuetzle and Perez (1983) estimated that an average of 12% of the 1-nitropyrene in diesel emissions collected on filters and using dilution tubes was formed on the filter during sampling. As will be discussed in more detail below, the nitro-PAH isomers observed in ambient particulate samples have very different isomer distributions than those found in diesel particulate extracts (Arey et al., 1987; 1989b; 1990a; Atkinson et al., 1988).

It is interesting to note that recent work (Ross et al., 1987) suggests that dinitropyrenes observed in diesel exhaust (Pederson and Siak, 1981; Nakagawa et al., 1983; Schuetzle, 1983; Schuetzle and Perez, 1983) are the result of direct nitration of pyrene rather than further nitration of 1-nitropyrene. However, Lee et al. (1989) suggest that dinitropyrene formation may be a collection artifact, being formed from 1-nitropyrene nitration by NO_2.

C. Physical Loss Processes

The particles with which the PAH and PAH-derivatives are associated undergo wet and dry deposition. The average atmospheric lifetimes for particles due to dry deposition are a function of the particle diameter, as shown in Table 3 (Graedel and Weschler, 1981). As discussed above, the particles emitted from diesel-fueled vehicles have mass-median aerodynamic diameters of ~0.1-0.3 μm, and hence the atmospheric lifetimes of these particles due to dry deposition are expected to be of the order of ~5-15 days.

In the case of wet deposition, a washout ratio of particles W_p, defined as,

$$W_p = C_{rain}/C_{air}$$

relates the particle concentration in the rain (C_{rain}) to that in the ambient air (C_{air}). The deposition rate, F, is given by,

$$F = W_p \, J \, C_{air}$$

where J is the precipitation rate. For particles of 0.1-10 μm diameter and for particle-associated organics such as the polychlorinated biphenyls (PCBs) and the C_{20}-C_{23} n-alkanes the washout ratio W_p is $10^{5\pm1}$ (Eisenreich et al., 1981; Ligocki et al., 1985a). With a washout ratio of this magnitude, essentially complete scavenging of the particles and their associated organics occurs during a rain event (Leuenberger et al., 1985). Of course, rain-out is an episodic event which, in California, will lead to generally shorter lifetimes of the particle-associated PAH and PAH-derivatives in the winter months than during the summertime.

Table 3. Average Atmospheric Lifetimes for Particles Due to Dry Deposition (From Graedel and Weschler, 1981)

Diameter (μm)	Lifetime (days)
0.002	0.01
0.02	1
0.2	10
2	10
20	1
200	0.01

Thus, considering only its physical atmospheric removal processes, the lifetime of particle-associated PAH and PAH-derivatives due to particle dry deposition is expected to be around 5-15 days, with an additional efficient, but episodic, removal process involving the rain-out of particles.

D. Gas-Phase Loss Processes of PAH and PAH-Derivatives

As noted in the Introduction, the PAH and PAH-derivatives present, at least partially, in the gas phase can undergo wet and dry deposition, photolysis and reaction with OH and NO_3 radicals and O_3. To date, there is no evidence for the occurrence of other gas-phase reactions (for example, with NO_2, HNO_3 or SO_2) for the PAH or nitroarenes (the only PAH-derivatives for which experimental data are available). In this Section, the available kinetic and product data concerning photolysis and reactions with OH and NO_3 radicals and O_3 are presented and discussed.

1. Wet Deposition of Gas-Phase PAH and PAH-Derivatives

Experimental data concerning the washout ratios W_g, of gas-phase PAH, where

$$W_g = [PAH]_{rain}/[PAH]_{gas}$$

have been obtained and reported by Ligocki et al. (1985b). The values obtained are given in Table 4. From concurrent measurements of PAH and

Table 4. Washout Ratios for Gas-Phase PAH (from Ligocki et al., 1985b)

PAH	Molecular Weight	Washout ratio W (at 281 K)
Naphthalene	128	250 ± 73
1-Methylnaphthalene	142	330 ± 100
2-Methylnaphthalene	142	250 ± 78
Acenaphthylene	152	1600 ± 500
Acenaphthene	154	1000 ± 310
Fluorene	166	1500 ± 390
Phenanthrene	178	3400 ± 740
Anthracene	178	1900 ± 600
Methylphenanthrenes	192	2500 ± 800
Fluoranthene	202	6300 ± 2000
Pyrene	202	5900 ± 1800
Benz[a]anthracene	228	12000 ± 4900
Chrysene	228	18000 ± 6500
Benzo[e]pyrene	252	5800
Benzo[b+j+k]fluoranthene	252	7400 ± 1300
9-Fluorenone	180	11000 ± 2200
9,10-Anthracenedione	208	27000 ± 7000

PAH-derivative concentrations in air and in rainwater, Ligocki et al. (1985a) concluded that the PAH of molecular weight <252 underwent wet deposition primarily from the gas phase, while the ≥252 molecular weight (MW) PAH underwent wet deposition primarily from the particle phase. This conclusion is in reasonable agreement with the review of Bidleman (1988), which concludes that wet deposition from the gas phase dominates for PAH of MW ≤202 and wet deposition from the particle phase dominates for PAH of MW ≥228. These conclusions of Ligocki et al. (1985b) and Bidleman (1988) are consistent with the PAH of MW ≤202 being predominantly in the gas phase with relatively low washout ratios (10^2-10^4), while the PAH of MW ≥252 reside on or in particles which generally have higher washout ratios ($10^{5\pm1}$). In comparison with the washout ratios of the very efficiently removed particles, the washout ratios of 10^2-10^4 for the gas-phase PAH suggest that wet deposition will not be a major tropospheric removal process for the PAH.

Dry deposition of gas-phase PAH is expected to be of minor importance (see, for example, Eisenreich et al., 1981).

2. Reaction with the OH Radical

The available rate constant data for the gas-phase reactions of the OH radical with PAH and PAH-derivatives have been evaluated and reviewed by Atkinson (1989). The rate constant data are given in Table 5. For most of the PAH and PAH-derivatives for which data are available, only single studies have been carried out, and no firm recommendations were made by Atkinson (1989) for these compounds. For biphenyl, naphthalene and phenanthrene, sufficient data are available that recommendations were made.

Biphenyl. The rate constants of Zetzsch (1982), Atkinson et al. (1984), Atkinson and Aschmann (1985) and Klöpffer et al. (1986), all obtained at room temperature, are in generally good agreement, although the rate constant determined by Zetzsch (1982) (which required knowledge of the vapor pressure of biphenyl) is lower by ~25% than the other values. Since no details are available concerning the study of Klöpffer et al. (1986), the rate constant from that study is not used in the evaluation. A unit-weighted average of the room temperature rate constants of Zetzsch (1982), Atkinson et al. (1984) and Atkinson and Aschmann (1985) leads to the recommendation of

Table 5. Rate Constants k and Temperature-Dependent Parameters for the Gas-Phase Reactions of the OH Radical with PAH and PAH-Derivatives at the High Pressure Limit (from Atkinson, 1989)

Aromatic	$10^{12} \times A$ (cm^3 molecule^{-1} s^{-1})	B (K)	$10^{12} \times k_1$ (cm^3 molecule^{-1} s^{-1})	at T (K)	Technique	Reference	Temperature range covered (K)
Biphenyl			5.8 ± 0.8	296	FP-RF	Zetzsch (1982)	
			7.61 ± 0.67	294 ± 1	RR [relative to k(n-nonane)$_1$ = 1.01×10^{-11}][a]	Atkinson et al. (1984)	
			8.32 ± 0.75	295 ± 1	RR [relative to k(cyclohexane) = 7.43×10^{-12}][a]	Atkinson and Aschmann (1985)	
			8.0	300	RR [relative to k(ethene) = 8.44×10^{-12}][a]	Klöpffer et al. (1986)	
1,4-Naphtho-quinone			3.1 ± 1.2	298 ± 2	RR [relative to k(cyclohexane) = 7.49×10^{-12}][a]	Atkinson et al. (1989a)	
Fluorene			13.0	300	RR [relative to k(ethene) = 8.44×10^{-12}][a]	Klöpffer et al. (1986)	
Naphthalene			18.6 ± 1.0	300	LP-RF	Lorenz and Zellner (1983, 1984)	300-873
			14.6 ± 5.0	337			
			11.0 ± 4.4	358			
			10.1 ± 4.0	378 ± 2			
			11.6 ± 3.0	404			
	2.3 ± 1.5	-640 ± 300 (300-407 K)	10.5 ± 4.0	407			

Table 5 (continued) - 2

Aromatic	10^{12} x A (cm^3 molecule^{-1} s^{-1})	B (K)	10^{12} x k (cm^3 molecule^{-1} s^{-1})	at T (K)	Technique	Reference	Temperature range covered (K)
			6.3 ± 2.0	452			
			4.3 ± 1.5	476			
			1.3 ± 0.5	502			
			1.2 ± 0.4	525 ± 1			
			0.7 ± 0.2	528			
			0.6 ± 0.1	531			
			1.1 ± 0.1	636			
			1.1 ± 0.2	665			
			1.4 ± 0.2	727			
	50	2500 (636-873 K)	3.0 ± 0.5	873			
			22.8 ± 1.6	294 ± 1	RR [relative to k(n-nonane) = 1.01×10^{-11}][a]	Atkinson et al. (1984)	
			23.5 ± 0.6	298 ± 1	RR [relative to k(propene) = 2.63×10^{-11}][a]	Biermann et al. (1985)	
			25.9 ± 2.4	295 ± 1	RR [relative to k(2-methyl-1,3-butadiene) = 1.02×10^{-10}][a]	Atkinson and Aschmann (1986)	
			21.6	300	RR [relative to k(ethene) = 8.44×10^{-12}][a]	Klöpffer et al. (1986)	
1-Methyl-naphthalene			53.0 ± 4.8	298 ± 2	RR [relative to k(2-methyl-1,3-butadiene) = 1.01×10^{-10}][a]	Atkinson and Aschmann (1987)	

Table 5 (continued) - 3

Aromatic	10^{12} x A (cm^3 molecule^{-1} s^{-1})	B (K)	10^{12} x k (cm^3 molecule^{-1} s^{-1})	at T (K)	Technique	Reference	Temperature range covered (K)
2-Methylnaphthalene			52.3 ± 4.2	295 ± 1	RR [relative to k(2-methyl-1,3-butadiene) = 1.02 x 10^{-10}][a]	Atkinson and Aschmann (1986)	
1-Nitronaphthalene			5.4 ± 1.8	298 ± 2	RR [relative to k(cyclohexane) = 7.49 x 10^{-12}][a]	Atkinson et al. (1989a)	
2-Nitronaphthalene			5.6 ± 0.9	298 ± 2	RR [relative to k(cyclohexane) = 7.49 x 10^{-12}][a]	Atkinson et al. (1989a)	
2,3-Dimethylnaphthalene			76.8 ± 4.8	295 ± 1	RR [relative to k(2-methyl-1,3-butadiene) = 1.02 x 10^{-10}][a]	Atkinson and Aschmann (1986)	
2-Methyl-1-nitronaphthalene			<8.3	298 ± 2	RR [relative to k(cyclohexane) = 7.49 x 10^{-12}][a]	Arey et al. (1990b)	
1,4-Dichloronaphthalene			5.8	300	RR [relative to k(toluene) = 5.91 x 10^{-12}][a]	Klöpffer et al. (1986)	
Acenaphthene			58.4	300	RR [relative to k(ethene) = 8.44 x 10^{-12}][a]	Klöpffer et al. (1986)	
			103 ± 13	296 ± 2	RR [relative to k(2,3-dimethyl-2-butene) = 1.11 x 10^{-10}][a]	Atkinson and Aschmann (1988)	

Table 5 (continued) - 4

Aromatic	10^{12} x A (cm^3 molecule^{-1} s^{-1})	B (K)	10^{12} x k (cm^3 molecule^{-1} s^{-1})	at T (K)	Technique	Reference	Temperature range covered (K)
Acenaphthylene			110 ± 11	296 ± 2	RR [relative to k(2,3-dimethyl-2-butene) = 1.11 x 10^{-10}][a]	Atkinson and Aschmann (1988)	
Phenanthrene			15.6 ± 2.0	338	LP-RF	Lorenz and Zellner (1984)	338-748
			16.1 ± 2.0	355			
			19.1 ± 2.5	387			
			12.0 ± 1.7	399			
			8.3 ± 0.8	431			
			4.0 ± 0.7	492			
			2.8 ± 0.7	526			
			1.2 ± 0.2	597			
			1.2 ± 0.4	648			
			2.2 ± 0.5	748			
			34 ± 12	298 ± 1	RR [relative to k(propene) = 4.85 x $10^{-12}e^{504/T}$][a]	Biermann et al. (1985)	298-319
			28 ± 6	319 ± 1			
Anthracene			112 ± 9	325 ± 1	RR [relative to k(propene) = 2.29 x 10^{-11}][a]	Biermann et al. (1985)	

[a]From the recommendations of Atkinson (1989).

$$k(\text{biphenyl}) = 7.2 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K},$$

with an estimated overall uncertainty of ±30%. This rate constant is that for OH radical addition to the aromatic rings. At temperatures $\gtrsim$400 K the OH-biphenyl adduct will rapidly thermally decompose and only H-atom abstraction from the C-H bonds of the aromatic rings will be observed.

Naphthalene. The available rate constants obtained at, or close to, the high-pressure limit are given in Table 5. Lorenz and Zellner (1983) have shown that at 378 ± 2 K the rate constant for this reaction is in the fall-off region between second- and third-order kinetics below ~50 Torr total pressure of helium, but that no such fall-off behavior is observed at 525 ± 1 K.

At temperatures ≤410 K the rate constants obtained by Lorenz and Zellner (1983, 1984), Atkinson et al. (1984), Biermann et al. (1985), Atkinson and Aschmann (1986) and Klöpffer et al. (1986) are in good agreement (the rate constant of Klöpffer et al. (1986) was not used in the evaluation because of a lack of details). A unit-weighted least-squares analysis of the data of Lorenz and Zellner (1983, 1984), Atkinson et al. (1984), Biermann et al. (1985) and Atkinson and Aschmann (1986) yields the recommended Arrhenius expression of

$$k(\text{naphthalene, } T \leq 410 \text{ K}) = (1.07^{+1.14}_{-0.55}) \times 10^{-12} \, e^{(895 \pm 239)/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 294-407 K, where the indicated errors are two least-squares standard deviations, and

$$k(\text{naphthalene}) = 2.16 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

at 298 K, with an estimated overall uncertainty of ±30% at 298 K.

Phenanthrene. The available rate constants of Lorenz and Zellner (1984) and Biermann et al. (1985) are given in Table 5. The rate constants obtained by Biermann et al. (1985) from a relative rate study are consistent with the higher temperature (T ≥338 K) data of Lorenz and Zellner (1984). For the temperature range ≤410 K (the same as for

naphthalene) a unit-weighted least-squares analysis of the data of Lorenz and Zellner (1984) and Biermann et al. (1985) yields the recommendation of

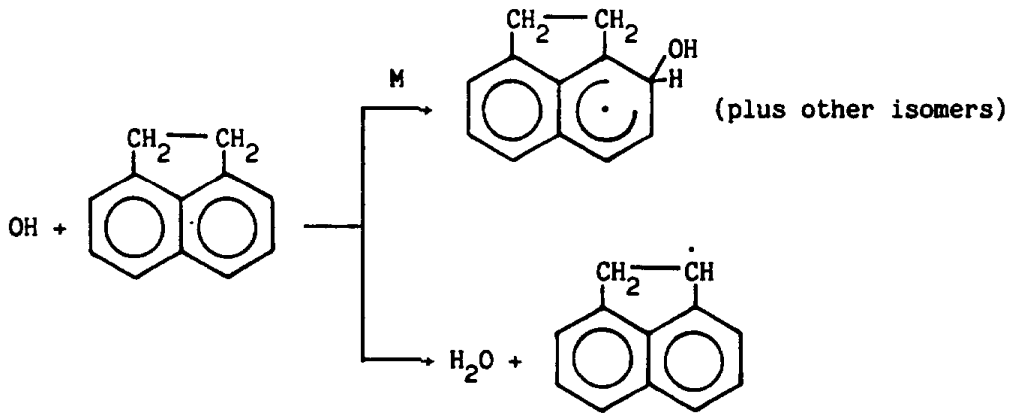
$$k(\text{phenanthrene};\ T \leq 410\ K) = (1.02^{+5.41}_{-0.86}) \times 10^{-12}\ e^{(1021 \pm 634)/T}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$$

over the temperature range 298-399 K, where the indicated errors are two least-squares standard deviations, and

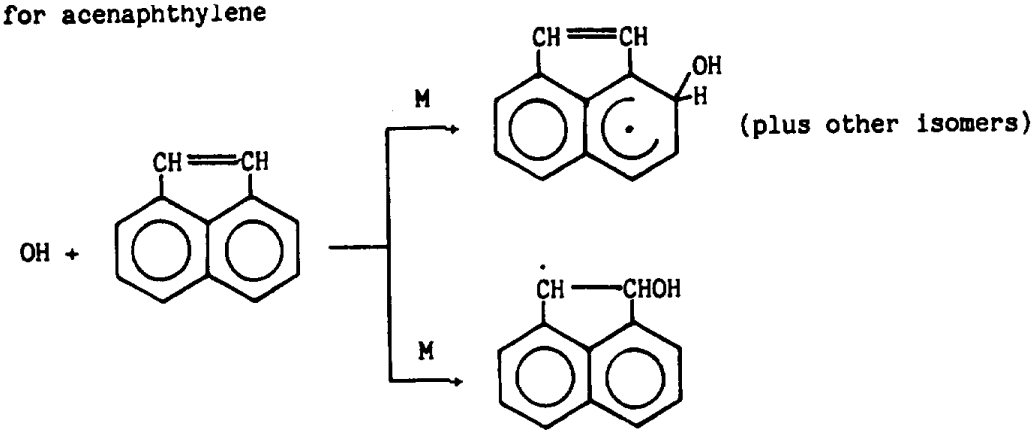
$$k(\text{phenanthrene}) = 3.1 \times 10^{-11}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}\ \text{at 298 K},$$

with an estimated overall uncertainty at 298 K of ± a factor of 2.

Reaction Mechanisms. As discussed by Atkinson (1986, 1989) the OH radical reactions with the PAH and PAH-derivatives proceed by two reaction pathways; namely OH radical addition to the aromatic ring to form an initially energy-rich hydroxycyclohexadienyl-type radical and OH radical interaction with the substituent groups, either through H atom abstraction from C-H or O-H bonds or OH radical addition to >C=C< bonds. For example, for acenaphthene



and for acenaphthylene



These OH radical reactions are essentially at the high pressure limits at room temperature and atmospheric pressure. For the alkyl-substituted PAH such as 1- and 2-methylnaphthalene, 2,3-dimethylnaphthalene and (probably) acenaphthene, the reaction pathway involving OH radical addition to the aromatic ring dominates under atmospheric conditions (Atkinson, 1989). For those PAH containing unsaturated cyclopenta-fused rings (acenaphthylene and acephenanthrylene), OH radical addition to the cyclopenta-fused ring >C=C< bond may be significant.

The products of these OH radical-initiated reactions are not well understood. The observed products of the OH radical-initiated reactions (in the presence of NO_x) of naphthalene and biphenyl are hydroxy- and nitro-arenes (Atkinson et al., 1987). The yields of the hydroxyarenes are significantly higher than those of the nitroarenes, being 7% and 4% for 1- and 2-naphthol, respectively, in comparison to ~0.3% each for 1- and 2-nitronaphthalene. Similarly, the yield of 2-hydroxybiphenyl from biphenyl is 20% (with much lower amounts of 3- and 4-hydroxybiphenyl also being produced), while the single nitro-derivative observed is 3-nitrobiphenyl in ~5% yield.

The specific nitroarene isomers formed, and their product yields, from the gas-phase OH radical-initiated reactions of the 2- to 4-ring PAH 1- and 2-methylnaphthalene (Zielinska et al., 1989a), biphenyl (Atkinson et al., 1987; Arey et al., 1989b), acenaphthene (Arey et al., 1989b), acenaphthylene (Arey et al., 1989b), phenanthrene (Arey et al., 1989b), anthracene (Arey et al., 1989b), acephenanthrylene (Zielinska et al.,

1988), fluoranthene (Arey et al., 1986; Atkinson et al., 1990a) and pyrene (Arey et al., 1986; Atkinson et al., 1990a) are given in Table 6. Preliminary results from a recent study of the gas-phase OH radical-initiated reaction of fluorene shows that the major nitroarene product from this PAH is 3-nitrofluorene with a yield of ~1% (Arey, Helmig and Atkinson, unpublished results).

The available product data for the monocyclic aromatic hydrocarbons and biphenyl (Atkinson et al., 1987, 1989b, 1990b) indicate that the nitroarene product yields do not extrapolate to zero at low NO_2 concentrations, and hence the nitroarene formation yields determined under laboratory conditions (see Table 6) are believed to be applicable to ambient atmospheric conditions. The nitroarene product formation yields are in all cases low, ranging from ~0.5-5%, and as noted above, the hydroxy-PAH yields for naphthalene and biphenyl are a factor of ~5-10 higher than their nitroarene yields. It is important to note that the majority of the OH radical-initiated reaction products of the PAH remain unidentified. While there are uncertainties about the reaction mechanisms, a recently postulated mechanism (Atkinson et al., 1989b) for the reaction of the OH radical in the presence of NO_x with fluoranthene which is consistent with our recent product data is shown in Figure 1.

Note that the nitroarenes formed from the OH radical-initiated reactions of the PAH (Table 6) are often isomers distinct from those observed in diesel exhaust particles. Thus as noted above, the most abundant nitro-isomers of pyrene, fluorene and fluoranthene observed in diesel exhaust are 1-nitropyrene, 2-nitrofluorene and 3-nitrofluoranthene, respectively, while the isomers formed from the gas-phase OH radical-initiated reactions of these PAH are 2-nitropyrene, 3-nitrofluorene and 2-nitrofluoranthene, respectively.

Table 6. Nitroarene Product Data for the Gas-Phase OH and NO_3 Radical-Initiated Reactions of PAH (Adapted from Arey et al., 1989b; Atkinson et al., 1990a)

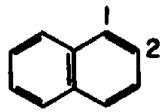
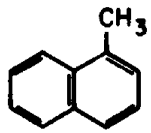
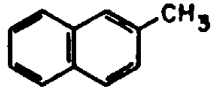
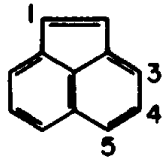
PAH	Structure	Nitroarene Formed (Yield) in Reaction with	
		OH	NO_3
Naphthalene		1-Nitronaphthalene (0.3%) 2-Nitronaphthalene (0.3%)	1-Nitronaphthalene (17%) 2-Nitronaphthalene (7%)
1-Methylnaphthalene[a]		1-Methyl-5-nitronaphthalene[b] 1-Methyl-4-nitronaphthalene[b] 1-Methyl-6-nitronaphthalene 1-Methyl-3-nitronaphthalene 1-Methyl-7-nitronaphthalene 1-Methyl-2-nitronaphthalene[b] 1-Methyl-8-nitronaphthalene[b] Total Yield (~0.4%)	1-Methyl-3-nitronaphthalene 1-Methyl-5-nitronaphthalene 1-Methyl-4-nitronaphthalene 1-Methyl-8-nitronaphthalene 1-Methyl-6-nitronaphthalene 1-Methyl-7-nitronaphthalene 1-Methyl-2-nitronaphthalene Total Yield (~30%)
2-Methylnaphthalene[a]		2-Methyl-5-nitronaphthalene 2-Methyl-6-nitronaphthalene 2-Methyl-7-nitronaphthalene 2-Methyl-4-nitronaphthalene 2-Methyl-8-nitronaphthalene 2-Methyl-3-nitronaphthalene 2-Methyl-1-nitronaphthalene[b] Total Yield (~0.2%)	2-Methyl-4-nitronaphthalene 2-Methyl-1-nitronaphthalene 2-Methyl-5-nitronaphthalene 2-Methyl-8-nitronaphthalene 2-Methyl-3-nitronaphthalene 2-Methyl-7-nitronaphthalene 2-Methyl-6-nitronaphthalene Total Yield (~30%)
Acenaphthylene		4-Nitroacenaphthylene[c] (2%)	None observed[d]

Table 6 (continued) - 2

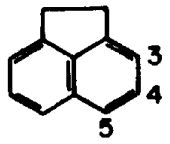
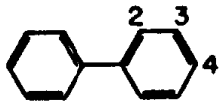
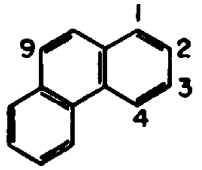
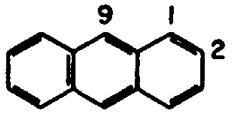
PAH	Structure	Nitroarene Formed (Yield) in Reaction with OH	Nitroarene Formed (Yield) in Reaction with NO_3
Acenaphthene[a]		5-Nitroacenaphthene 3-Nitroacenaphthene 4-Nitroacenaphthene Total Yield (~0.2%)	4-Nitroacenaphthene (40%)[e] 3-Nitroacenaphthene (~2%)[e] 5-Nitroacenaphthene (~2%)[e]
Biphenyl		3-Nitrobiphenyl (5%)	No reaction observed
Phenanthrene		Two isomers (not 9-nitrophenanthrene) Total Yield (≤0.1%)	Four isomers (including 9-nitrophenanthrene) Total Yield (<1%)
Anthracene		1-Nitroanthracene[f] 2-Nitroanthracene Total Yield (~0.2%)	1-Nitroanthracene[f] 2-Nitroanthracene Total Yield (<2%)

Table 6 (continued) - 3

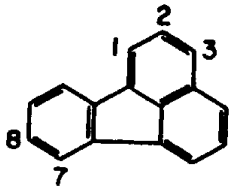
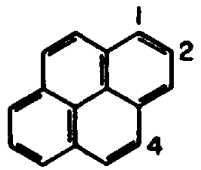
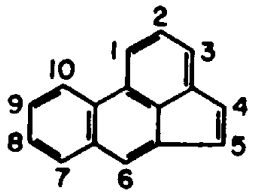
PAH	Structure	Nitroarene Formed (Yield) in Reaction with	
		OH	NO_3
Fluoranthene		2-Nitrofluoranthene (3%) 7-Nitrofluoranthene (1%) 8-Nitrofluoranthene (0.3%)	2-Nitrofluoranthene (24%)
Pyrene		2-Nitropyrene (0.5%) 4-Nitropyrene (0.06%)	4-Nitropyrene (~0.06%)
Acephenanthrylene		Two isomers (not 4- or 5-nitro-acephenanthrylene) (~0.1%)	None observed

Table 6 (continued) - 4

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[a]Nitro-isomers listed in approximate order of decreasing yield.

[b]Formed, at least partially, as a sampling artifact by reaction of NO_2 and/or NO_2 + HNO_3.

[c]Presence of 1-nitroacenaphthylene attributed to artifact formation during sampling.

[d]NO_3 Radical reaction occurs by NO_3 radical addition to the cyclopenta-fused ring.

[e]Not expected to be formed in ambient air because of concurrent H atom abstraction from the cyclopenta-fused ring.

[f]Presence of 9-nitroanthracene attributed to artifact formation during sampling.

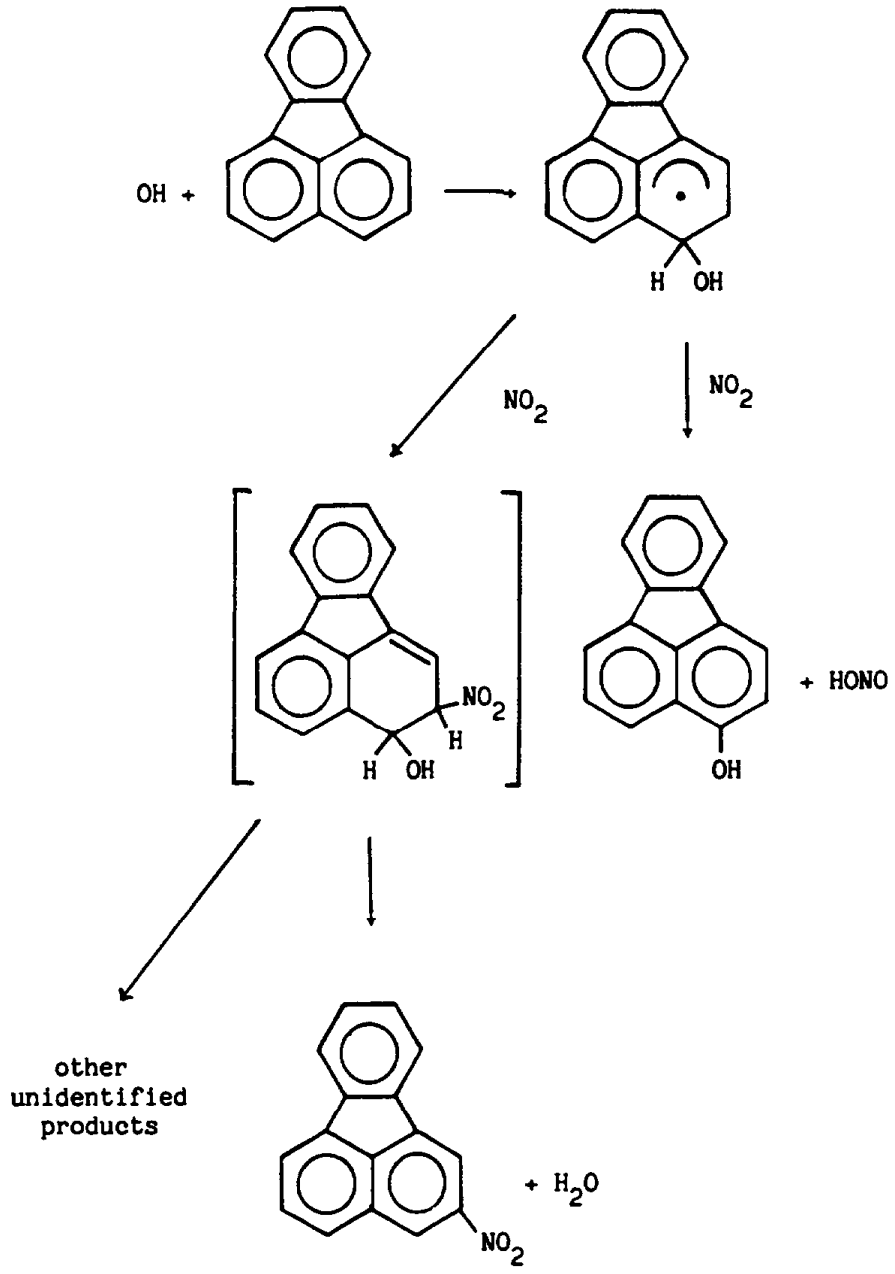


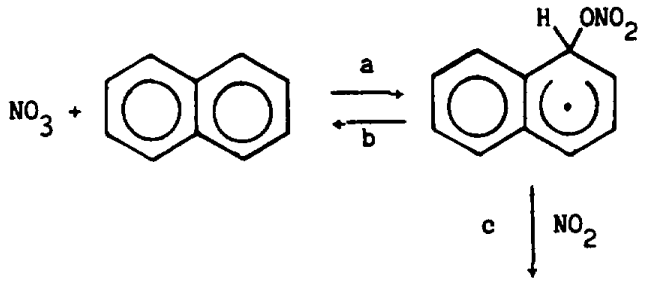
Figure 1. Reaction scheme for the OH radical-initiated reaction of fluoranthene in the presence of NO_x.

3. NO_3 Radical Reactions

Naphthalene and the alkyl-substituted naphthalenes are observed to react in N_2O_5 - NO_3 - NO_2 - air mixtures, in which NO_3 radicals are generated by the thermal decomposition of N_2O_5

$$N_2O_5 \rightarrow NO_3 + NO_2$$

The disappearance rates of the naphthalenes relative to those of the alkenes such as propene and trans-2-butene in these reaction mixtures as a function of the NO_2 concentration indicate that the PAH loss processes are kinetically equivalent to reaction with N_2O_5 (Pitts et al., 1985a; Atkinson et al., 1987; Atkinson and Aschmann, 1987, 1988; Atkinson et al., 1990c). As discussed by Atkinson and Aschmann (1988) and Atkinson et al. (1990c), this can be due to either an elementary reaction with N_2O_5 or to a complex reaction sequence involving initial addition of NO_3 to the aromatic rings to form a nitratocyclohexadienyl-type radical which then either back decomposes to reactants or reacts exclusively with NO_2

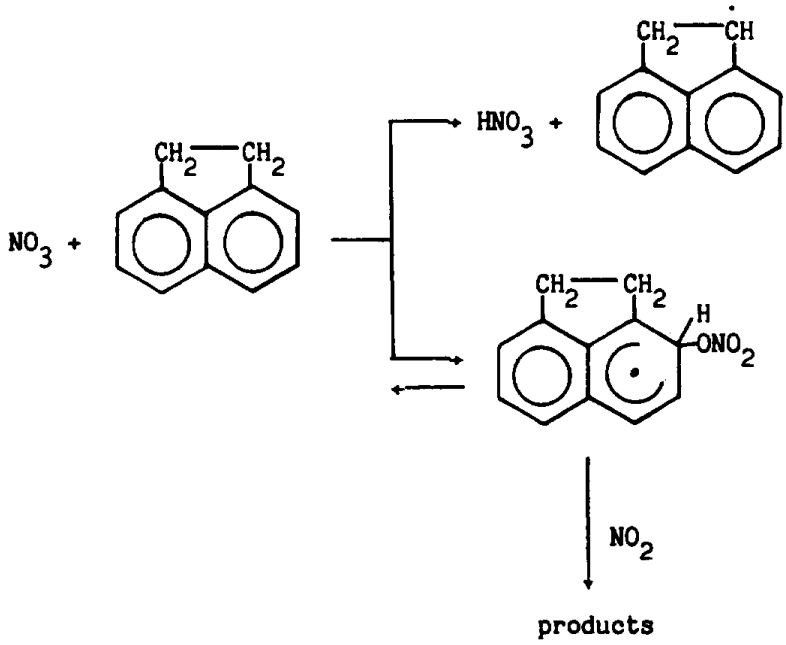


with the measured rate constant k_{obs} for reaction with the NO_3 radical being

$$k_{obs} = k_a k_c / k_b$$

A recent experimental study (Atkinson et al., 1990c) has shown that the reaction of naphthalene in N_2O_5 - NO_3 - NO_2 - air mixtures occurs by the initial addition of the NO_3 radical, rather than by an elementary reaction with N_2O_5, and the other PAH are expected to react in an analogous manner.

For those PAH containing substituent groups, a parallel reaction pathway involving NO_3 radical reaction with the substituent group(s) can also occur (Atkinson and Aschmann, 1988; Arey et al., 1989b), in addition to NO_3 radical addition to the aromatic ring. For example, for acenaphthene



and for acenaphthylene NO_3 radical addition to the cyclopenta-fused >C=C< bond is the dominant reaction pathway (Atkinson and Aschmann, 1988). Table 7 gives the available rate constant data for the NO_3 radical reactions which proceed by H-atom abstraction from, or NO_3 radical addition to, the substituent groups, and these reaction pathways are experimentally kinetically equivalent to an NO_3 radical reaction.

Table 8 gives the rate coefficients k_{obs} (where $k_{obs} = k_a k_c / k_b$) for the reactions of NO_3 radicals with the aromatic ring(s), and these reactions are experimentally kinetically equivalent to reaction with N_2O_5. The rate coefficients for a reaction with N_2O_5, $k_{N_2O_5}$, may be readily obtained from k_{obs} since $k_{N_2O_5} = k_{obs}/K$, where K is the equilibrium constant for the $NO_3 + NO_2 \rightleftarrows N_2O_5$ reactions and is given by (Atkinson, 1990a) $K = 1.26 \times 10^{-27} e^{11275/T}$ cm^3 $molecule^{-1}$ (3.41×10^{-11} cm^3 $molecule^{-1}$ at 298 K).

Table 7. Rate Constants k for the Gas-Phase Reactions of the NO_3 Radical with PAH

Aromatic	k (cm^3 $molecule^{-1}$ s^{-1})	at T (K)	Technique	Reference
1,4-Naphthoquinone	$<9.5 \times 10^{-16}$	298 ± 2	RR [relative to k(propene) $= 9.45 \times 10^{-15}$]^b	Atkinson et al. (1989a)
Acenaphthene	$(4.59 \pm 2.45) \times 10^{-13}$	296 ± 2	RR [relative to k(trans-2-butene) $= 3.89 \times 10^{-13}$]^b	Atkinson and Aschmann (1988)
Acenaphthylene	$(5.45 \pm 0.47) \times 10^{-12}$	296 ± 2	RR [relative to k(trans-2-butene) $= 3.89 \times 10^{-13}$]^b	Atkinson and Aschmann (1988)
1-Nitronaphthalene	$\leq 7.2 \times 10^{-15}$	298 ± 2	RR [relative to k(propene) $= 9.45 \times 10^{-15}$]^b	Atkinson et al. (1989a)
2-Nitronaphthalene	$\leq 7.3 \times 10^{-15}$	298 ± 2	RR [relative to k(propene) $= 9.45 \times 10^{-15}$]^b	Atkinson et al. (1989a)
2-Methyl-1-nitro-naphthalene	$(1.13 \pm 0.57) \times 10^{-14}$	298 ± 2	RR [relative to k(propene) $= 9.45 \times 10^{-15}$]^b	Arey et al. (1990b)

Table 8. Rate Constants $k_{obs} = k_a k_c / k_b$ for the Gas-Phase Reactions of the NO_3 Radical with PAH

Aromatic	$k_{obs} = k_a k_c / k_b$ (cm^6 $molecule^{-2}$ s^{-1})	at T (K)	Technique	Reference
Biphenyl	$<5 \times 10^{-30}$	298 ± 2	RR [relative to k_{obs}(naphthalene) $= 3.6 \times 10^{-28}$]	Atkinson et al. (1987)
Naphthalene	~(7-10) x 10^{-28}	298 ± 2	S-IR [relative to K ($NO_3 + NO_2 \rightleftharpoons N_2O_5$) $= 3.41 \times 10^{-11}$]	Pitts et al. (1985a)
	(4.77 ± 0.69) x 10^{-28}	298 ± 2	S-IR [relative to K($NO_3 + NO_2 \rightleftharpoons N_2O_5$) $= 3.41 \times 10^{-11}$]	Atkinson et al. (1987)
	3.31×10^{-28}	296 ± 2	RR [relative to k(propene) $= 9.45 \times 10^{-15}$]	Atkinson and Aschmann (1988)
	(1.28 ± 0.20) x 10^{-27}	272.0 ± 0.6	RR [relative to k(thiophene) $= 3.93 \times 10^{-14}$]	Atkinson et al. (1990a)
	(1.10 ± 0.27) x 10^{-27}	275.2 ± 0.6		
	(1.32 ± 0.25) x 10^{-27}	275.2 ± 0.6		
	(6.96 ± 1.73) x 10^{-28}	281.9 ± 0.6		
	(5.31 ± 1.18) x 10^{-28}	289.1 ± 0.6		

Table 8 (continued) - 2

Aromatic	$k_{obs} = k_a k_c / k_b$ (cm^6 $molecule^{-2}$ s^{-1})	at T (K)	Technique	Reference
	$(3.64 \pm 1.11) \times 10^{-28}$	296.3 ± 0.6		
	$(3.66 \pm 1.26) \times 10^{-28}$	296.9 ± 0.6		
Naphthalene-d_8	$(4.4 \pm 0.4) \times 10^{-28}$	298 ± 2	RR [relative to k_{obs}(naphthalene) = 3.6×10^{-28}]	Atkinson et al. (1990a)
1-Methyl-naphthalene	$(8.4 \pm 1.0) \times 10^{-28}$	298 ± 2	RR [relative to k_{obs}(naphthalene) = 3.6×10^{-28}][a]	Atkinson and Aschmann (1987)
	7.0×10^{-28}	296 ± 2	RR [relative to k(<u>trans</u>-2-butene) = 3.89×10^{-13}]	Atkinson and Aschmann (1988)
2-Methyl-naphthalene	$(1.07 \pm 0.16) \times 10^{-27}$	298 ± 2	RR [relative to k_{obs}(naphthalene) = 3.6×10^{-28}]	Atkinson and Aschmann (1987)
	1.09×10^{-27}	296 ± 2	RR [relative to k(propene) = 9.45×10^{-15}]	Atkinson and Aschmann (1988)

Table 8 (continued) - 3

Aromatic	$k_{obs} = k_a k_c / k_b$ (cm^6 $molecule^{-2}$ s^{-1})	at T (K)	Technique	Reference
2,3-Dimethyl-naphthalene	$(1.48 \pm 0.44) \times 10^{-27}$	298 ± 2	RR [relative to k_{obs}(naphthalene) = 3.6×10^{-28}]	Atkinson and Aschmann (1987)
	1.61×10^{-27}	296 ± 2	RR [relative to k(propene) = 9.45×10^{-15}]	Atkinson and Aschmann (1988)
Acenaphthene	$(1.65 \pm 0.38) \times 10^{-27}$	296 ± 2	RR [relative to k(trans-2-butene) = 3.89×10^{-13}]	Atkinson and Aschmann (1988)
1-Nitro-naphthalene	$(3.02 \pm 1.42) \times 10^{-29}$	298 ± 2	RR [relative to k(propene) = 9.45×10^{-15}]	Atkinson et al. (1989a)
2-Nitro-naphthalene	$(2.74 \pm 1.14) \times 10^{-29}$	298 ± 2	RR [relative to k(propene) = 9.45×10^{-15}]	Atkinson et al. (1989a)
1,4-Naphtho-quinone	$< 8.5 \times 10^{-30}$	298 ± 2	RR [relative to k(propene) = 9.45×10^{-15}]	Atkinson et al. (1989a)

Table 8 (continued) - 4

Aromatic	$k_{obs} = k_a k_c / k_b$ (cm^6 $molecule^{-2}$ s^{-1})	at T (K)	Technique	Reference
2-Methyl-1-nitro naphthalene	$(2.74 \pm 1.80) \times 10^{-29}$	298 ± 2	RR [relative to k(propene) = 9.45×10^{-15}]	Arey et al. (1990b)
Fluoranthene	~4.7×10^{-28}	298 ± 2	RR [relative to k_{obs}(naphthalene) = 3.6×10^{-28}]	Atkinson et al. (1990a)
Pyrene	~1.4×10^{-27}	298 ± 2	RR [relative to k_{obs}naphthalene) = 3.6×10^{-28}]	Atkinson et al. (1990a)

The reactions which involve the initial addition of the NO_3 radical to the aromatic ring (termed hereafter an N_2O_5 reaction for simplicity) lead to the formation of nitroarenes (Pitts et al., 1985a; Sweetman et al., 1986; Atkinson et al., 1987, 1990a; Zielinska et al., 1989a; Arey et al., 1989b), and these nitroarene yield data are given in Table 6. The reaction routes involving NO_3 radical interaction with the substituent group(s) do not lead to the formation of nitroarenes, as expected from the likely subsequent chemistry (Atkinson, 1990b). The other products of these gas-phase "N_2O_5" reactions of the PAH are presently not known with any certainty, although they may include hydroxynitro-PAH.

4. O_3 Reactions

The available rate constant data for reaction of PAH with O_3 are given in Table 9. Only for acenaphthylene has gas-phase reaction been observed (Atkinson and Aschmann, 1988), and reaction is also expected to occur for acephenanthrylene (Zielinska et al., 1988). Clearly, these PAH react with O_3 by addition of O_3 at the cyclopenta-fused ring >C=C< bond (Atkinson and Aschmann, 1988).

5. Photolysis

No evidence has been observed for the gas-phase photolysis of the 2-4 ring PAH (Atkinson et al., 1984; Biermann et al., 1985; Atkinson and Aschmann, 1986, 1988). However, photolysis of 1- and 2-nitronaphthalene and 2-methyl-1-nitronaphthalene has been observed under ambient outdoor sunlight conditions (Atkinson et al., 1989a; Arey et al., 1990b). Photolysis of 1-nitronaphthalene, 2-methyl-1-nitronaphthalene and the 2-, 7- and 8-nitrofluoranthenes (the nitrofluoranthenes being totally particle-associated under atmospheric conditions) have also been observed in an indoor chamber with blacklamp irradiation (Atkinson et al., 1989a, 1990a; Arey et al., 1990b), with the photolysis rates of the 1-nitronaphthalene and 2-methyl-1-nitronaphthalene in the indoor chamber being approximately an order of magnitude higher than under ambient conditions (Atkinson et al., 1989a; Arey et al., 1990b). The photolysis rates are given in Table 10.

6. Atmospheric Lifetimes of Gas-Phase PAH and PAH-Derivatives

The photolysis and reaction rate data given above can be combined with the ambient radiation flux and the ambient concentrations of OH and NO_3 radicals, NO_2 and O_3 to allow the estimation of the lifetimes of the

Table 9. Rate Constants for the Gas-Phase Reactions of PAH and PAH-Derivatives with O_3

Aromatic	k (cm^3 $molecule^{-1}$ s^{-1})	at T (K)	Reference
Naphthalene	$<2 \times 10^{-19}$	294 ± 1	Atkinson et al. (1984)
	$<3 \times 10^{-19}$	295 ± 1	Atkinson and Aschmann (1986)
1-Methylnaphthalene	$<1.3 \times 10^{-19}$	298 ± 2	Atkinson and Aschmann (1987)
2-Methylnaphthalene	$<4 \times 10^{-19}$	295 ± 1	Atkinson and Aschmann (1986)
2,3-Dimethylnaphthalene	$<4 \times 10^{-19}$	295 ± 1	Atkinson and Aschmann (1986)
Biphenyl	$<2 \times 10^{-19}$	294 ± 1	Atkinson et al. (1984)
Acenaphthene	$<5 \times 10^{-19}$	296 ± 2	Atkinson and Aschmann (1988)
Acenaphthylene	5.5×10^{-16}	296 ± 2	Atkinson and Aschmann (1988)
1-Nitronaphthalene	$<6 \times 10^{-19}$	298 ± 2	Atkinson et al. (1989a)
2-Nitronaphthalene	$<6 \times 10^{-19}$	298 ± 2	Atkinson et al. (1989a)
2-Methyl-1-nitronaphthalene	$<3 \times 10^{-19}$	298 ± 2	Arey et al. (1990b)
1,4-Naphthoquinone	$<2 \times 10^{-19}$	298 ± 2	Atkinson et al. (1989a)

Table 10. Measured Photolysis Rates, k_{phot}, of PAH and PAH-Derivatives in a 6400 Liter Indoor Teflon Chamber with Blacklight Irradiation and Outdoors in a 1000 Liter Outdoor Teflon Chamber with Sunlight Irradiation[a]

Aromatic	$10^4 \times k_{phot}$ (s^{-1})	
	Indoors	Outdoors
1-Nitronaphthalene	15.9 ± 1.1	1.37 ± 0.10
2-Nitronaphthalene	≤2	1.06 ± 0.08
1,4-Naphthoquininone	1.1 ± 0.8	~0.9
2-Methyl-1-nitronaphthalene	37 ± 7	1.1 ± 0.3
3-Nitrobiphenyl	<0.17	
NO_2	78	43

[a]From Atkinson et al. (1989a) and Arey et al. (1990b).

PAH and PAH-derivatives with respect to each of these tropospheric loss processes. These lifetime data are given in Table 11. For the PAH not containing cyclopenta-fused rings, the dominant tropospheric loss process is by reaction with the OH radical, with calculated lifetimes of 1 day or less (note that OH radical reaction only occurs during daylight hours). The PAH containing cyclopenta-fused rings such as acenaphthene, acenaphthylene and acephenanthrylene are expected to also react with NO_3 radicals at a significant rate. (Note that NO_3 radical addition to the fused rings of the PAH is not significant as a tropospheric loss process for the PAH.) PAH having unsaturated cyclopenta-fused rings, such as acenaphthylene, acephenanthrylene and cyclopenta[cd]pyrene (MW 226), are expected to react with O_3 at a significant rate.

In contrast to O_3 and the OH radical, which are ubiquitous at reasonably consistent (on a day-to-day level) ambient concentrations (see, for example, Logan, 1985; Prinn et al., 1987; Arey et al., 1989a), the ambient concentrations of the NO_3 radical in the lower troposphere over continental areas exhibit large variations, with the mixing ratios ranging

Table 11. Calculated Atmospheric Lifetimes of PAH and PAH-Derivatives Due to Photolysis and Gas-Phase Reaction with OH and NO_3 Radicals and O_3

PAH	Lifetime due to reaction with			
	OH[a]	NO_3[b]	O_3[c]	Photolysis[d]
Naphthalene	8.6 hr	100 days	>80 days	
1-Methylnaphthalene	3.5 hr	50 days	>125 days	
2-Methylnaphthalene	3.6 hr	40 days	>40 days	
2,3-Dimethylnaphthalene	2.4 hr	25 days	>40 days	
Biphenyl	2.1 days	>20 yr	>80 days	
Acenaphthene	1.8 hr	2.5 hr	>30 days	
Acenaphthylene	1.7 hr	13 min	~43 min	
Phenanthrene	6.0 hr			
Anthracene	1.4 hr			
Fluoranthene	~3.7 hr[e]	~85 days		
Pyrene	~3.7 hr[e]	~30 days		
1-Nitronaphthalene	2.9 days	3.6 yr	>28 days	1.7 hr
2-Nitronaphthalene	2.8 days	4.0 yr	>28 days	2.2 hr
1,4-Naphthoquinone	5.0 days	>100 days	>80 days	~2.6 hr
2-Methyl-1-nitro-naphthalene	>1.8 days	4.0 yr	>55 days	2.1 hr

[a]For a 12-hr daytime average OH radical concentration of 1.5×10^6 molecule cm^{-3} (Prinn et al., 1987).

[b]For a 12-hr average nighttime NO_3 radical concentration of 2.4×10^8 molecule cm^{-3} and an NO_2 concentration of 2.4×10^{12} molecule cm^{-3} (Atkinson et al., 1986).

[c]For a 24-hr average O_3 concentration of 7×10^{11} molecule cm^{-3} (Logan, 1985).

[d]For an average 12-hr daytime NO_2 photolysis rate of $J_{NO_2} = 5.2 \times 10^{-3}$ s^{-1}.

[e]Using estimated OH radical reaction rate constant of 5×10^{-11} cm^3 molecule^{-1} s^{-1} based on rate constant correlation with ionization potential (Biermann et al., 1985; Arey et al., 1990b; Atkinson et al., 1990a).

from <2 parts-per-trillion (ppt) to 430 ppt (Atkinson et al., 1986), and the ambient tropospheric concentration of the NO_3 radical at any given time (during nighttime) and place must be viewed as being uncertain by at least a factor of 10. Hence to a good approximation the dominant tropospheric removal process for the PAH is by daytime reaction with the OH radical, leading to lifetimes of ~8 hours or less.

As seen from the rate constant data given in Table 5 and from the calculated lifetimes in Table 11, the presence of the nitro- substituent group in the nitroarenes leads to a marked decrease in their reactivity towards the OH radical. To date kinetic and product studies have only been carried out for three gas-phase fused-ring nitroarenes (Atkinson et al., 1989a; Arey et al., 1990b), and photolysis will be the dominant tropospheric removal process for these compounds, with calculated lifetimes of ~2 hrs.

7. Evidence for Atmospheric Transformations of PAH

The recent ambient air measurement study of Arey et al. (1989a) provided clear evidence for the reactions of the volatile PAH with the OH radical, with the nighttime/daytime concentration ratios exhibiting a clear linear correlation with the OH radical reaction rate constant (Figure 2). From an estimate of the nighttime dilution rate, provided by the daytime/nighttime ratio of 3-nitrobiphenyl [a nitroarene believed to be formed only in the atmosphere from the daytime reaction of biphenyl with the OH radical in the presence of NO_x (Atkinson et al., 1987)], an average 12-hr daytime OH radical concentration of 2.2×10^6 molecule cm^{-3} (during August) was derived, uncertain to at least a factor of 2. This estimated OH radical concentration in an urban area is essentially identical to the annually averaged global tropospheric 12-hr daytime OH radical concentration of 1.5×10^6 molecule cm^{-3} (Prinn et al., 1987) and provides very strong evidence that the gas-phase PAH do react in the troposphere. Furthermore, as discussed in detail in the literature (Nielsen et al., 1984; Pitts et al., 1985b; Nielsen and Ramdahl, 1986; Sweetman et al., 1986; Arey et al., 1986, 1987, 1989a,b, 1990a; Ramdahl et al., 1986; Zielinska et al., 1988, 1989a,b; Atkinson et al., 1988), many of the nitroarenes observed in ambient air are only formed in the atmosphere through the gas-phase reactions of the 2-4 ring PAH. For example, nitroarene isomers observed both in OH radical-initiated reactions of the

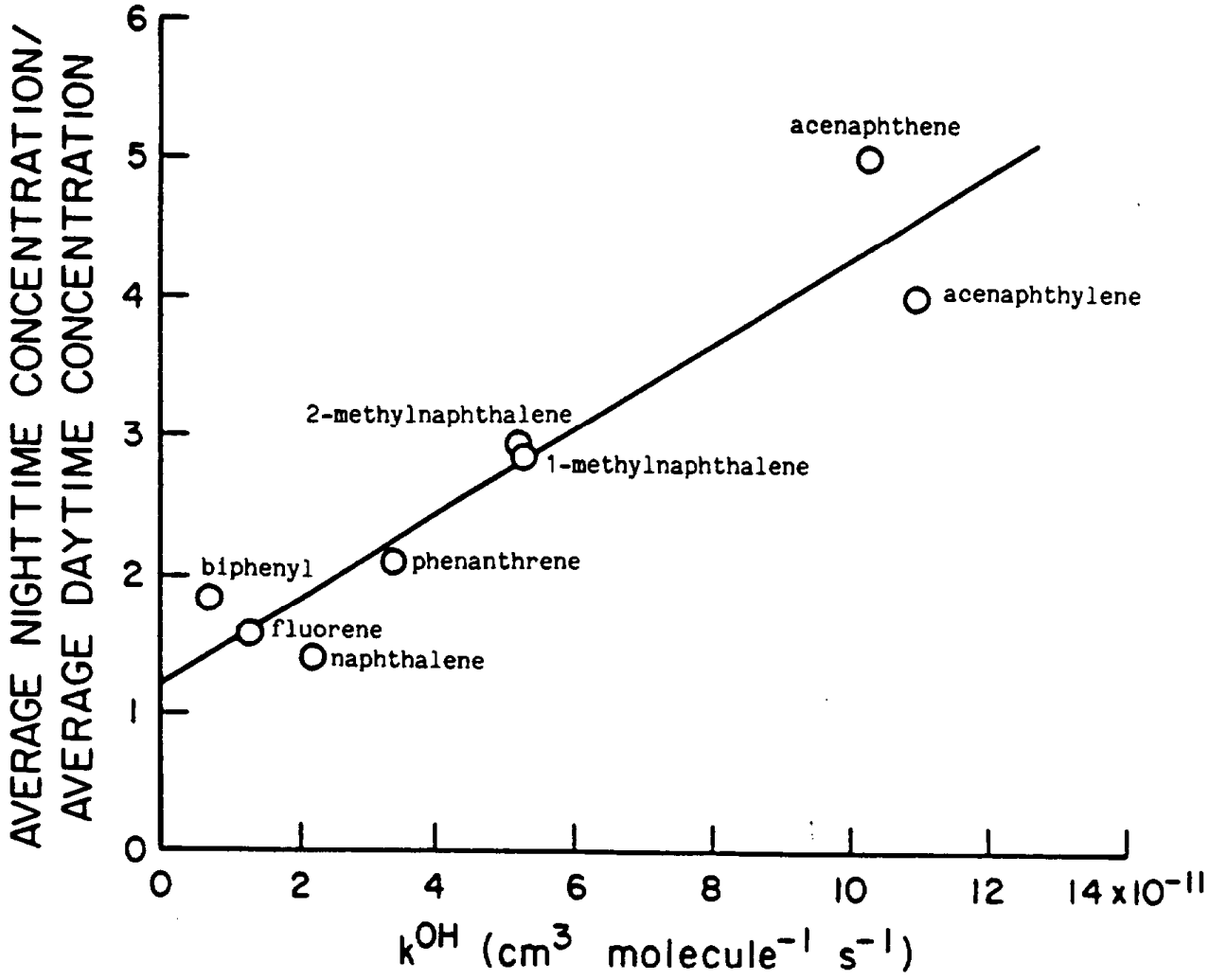


Figure 2. Plot of the average nighttime/average daytime concentration ratio for the volatile PAH measured in Glendora, CA against their OH radical reaction rate constants (Adapted from Arey et al. 1989a).

parent PAH and in ambient air samples, but not in diesel exhaust samples include: 2-nitrofluoranthene, 2-nitropyrene, 3-nitrobiphenyl and 2-methyl-7-nitronaphthalene (Arey et al., 1989b; Zielinska et al., 1989a).

The importance of atmospheric formation of nitroarenes is clear from a comparison of the calculated and observed 3-nitrobiphenyl, 1- + 2-nitronaphthalene, 2-nitrofluoranthene and 2-nitropyrene concentrations at two sites in southern California (Arey et al., 1990b). The predicted concentrations of these nitroarenes were calculated from the reaction rate constants (Table 5) and nitroarene product formation yields (Table 6) of the OH radical-initiated reactions of biphenyl, naphthalene, fluoranthene and pyrene, respectively, using estimated OH radical concentrations and the measured ambient parent PAH concentrations, and incorporating the photolysis loss of the nitronaphthalenes (Table 10). There was excellent agreement between the calculated nitroarene concentrations and the measured ambient concentrations of the nitroarenes at both sites (Table 12). Only the nitronaphthalenes are expected to be present in direct emissions such as diesel exhaust, and the slightly higher predicted than observed concentrations for the nitronaphthalenes suggests that atmospheric formation of these species dominates over their direct emission, at least at these two sites and at the time of the measurements.

Table 12. Ambient Nitroarene Concentrations at Torrance, CA in February 1986 and Glendora, CA, in August 1989 (Arey et al., 1990b)

	12-Hr Average Daytime Concentration ($ng\ m^{-3}$)			
	TORRANCE		GLENDORA	
	Measured	Calculated	Measured	Calculated
1- + 2-Nitronaphthalene	5.9	15	4.7	8.0
3-Nitrobiphenyl	6.0	2.4	1.0	1.2
2-Nitrofluoranthene	0.3	1.3	0.27	0.41
2-Nitropyrene	0.04	0.15	0.012	0.028

E. Adsorbed-Phase Loss Processes of PAH and PAH-Derivatives

In addition to the physical removal of the particles (Section C) with which the ≥MW 252 PAH and some fraction of the four-ring PAH are associated, the particle-associated PAH can also be transformed by a number of chemical processes in the adsorbed phase. These include photolysis and reaction with O_3, SO_2, NO_2 and/or HNO_3 and N_2O_5, and a large number of experimental investigations of these potential reaction pathways have been carried out (see, for example, Jager and Rakovic, 1974; Lane and Katz, 1977; Pitts et al., 1978, 1980, 1985c, 1986; Katz et al., 1979; Hughes et al., 1980; Jäger and Hanus, 1980; Korfmacher et al., 1980a,b, 1981; Peters and Seifert, 1980; Blau and Güsten, 1981; Butler and Crossley, 1981; Tokiwa et al., 1981; Daisey et al., 1982; Brorström et al., 1983; Grosjean et al., 1983; Nielsen et al., 1983; Ramdahl et al., 1984; Valerio et al., 1984, 1987; Van Vaeck and Van Cauwenberghe, 1984; Wu et al., 1984; Behymer and Hites, 1985, 1988; Benson et al., 1985; Brorström-Lunden and Lindskog, 1985; Kamens et al., 1985a,b, 1986, 1988, 1989; Lindskog et al., 1985; Wu and Niki, 1985; Yokley et al., 1985, 1986; Güsten, 1986; Ménard et al., 1986; Schuetzle and Frazier, 1986; Takeda and Teranishi, 1986; Cope and Kalkwarf, 1987; Holloway et al., 1987; Arey et al., 1988; Coutant et al., 1988; Nielsen, 1988; Greenberg, 1989). Interpretation of the experimental data obtained from the laboratory studies is rendered difficult due to the diverse substrates used, and in many cases conflicting data have been obtained. As discussed below, some differences may be attributed to the availability of the PAH for reaction, i.e., whether present as an adsorbed surface layer or included in the particles, or whether the particles were "freshly" emitted or were "aged" particles.

Benzo[a]pyrene (BaP) is a carcinogenic (IRAC, 1983) PAH often measured as a surrogate for all toxic PAH in ambient air particles. As noted in Section C, BaP (MW 252) will be particle-associated in ambient air and gas-phase reactions of BaP will be unimportant. Since the adsorbed-phase reactions of BaP have been studied more than those for any other single PAH, and in addition, BaP is considered to be among the more reactive PAH (Nielsen, 1984; Greenberg and Darack, 1987), it is appropriate to discuss the adsorbed-phase reactions of BaP in some detail. As can be seen from Table 13, which gives Nielsen's reactivity classifications toward electrophilic reactions, BaP is in Class 2 of a five class

Table 13. Reactivity Scale of PAH (Including Benzene and Biphenyl) in Electrophilic Reactions (from Nielsen, 1984)

Class 1:	benzo[a]tetracene, dibenzo[a,h]pyrene, pentacene, tetracene
Class 2:	anthanthrene, anthracene, benzo[a]pyrene, cyclopenta[c,d]pyrene, dibenzo[a,l]pyrene, dibenzo[a,i]pyrene, dibenzo[a,c]tetracene, perylene
Class 3:	benz[a]anthracene, benzo[g]chrysene, benzo[ghi]perylene, dibenzo[a,e]pyrene, picene, pyrene
Class 4:	benzo[c]chrysene, benzo[c]phenanthrene, benzo[e]pyrene, chrysene, coronene, dibenzanthracenes, dibenzo[e,l]pyrene
Class 5:	acenaphthylene, benzofluoranthenes, fluoranthene, indeno[1,2,3-cd]fluoranthene, indeno[1,2,3-cd]pyrene, naphthalene, phenanthrene, triphenylene
Class 6:	benzene, biphenyl

(Class 1 being the most reactive) scale. The PAH in Class 1 have not generally been observed in significant concentrations in diesel exhaust.

1. Reaction with O_3

Benzo[a]pyrene. The results obtained concerning the stability of BaP adsorbed onto surfaces in the presence of O_3 are disparate. Thus, Katz and coworkers (Katz et al., 1979) and Peters and Seifert (1980) observed that BaP reacted in the presence of ambient levels of O_3, and Pitts et al. (1980) identified the BaP-4,5-epoxide as a product of the reaction of O_3 with BaP deposited onto glass fiber filters. These studies indicated a BaP lifetime with respect to reaction with O_3 (at ambient concentrations, i.e., levels reached in polluted atmospheres) of the order of an hour. In contrast, Grosjean et al. (1983) observed no loss of BaP,

either deposited onto blank filters or on filters coated with ambient particles, fly ash or diesel particles, when exposed to 100 ppb of ozone for three hours. Brorström et al. (1983) observed no definitive evidence for losses of BaP (or other PAH) under high-volume sampling conditions with the addition of 200 ppb of O_3. However, it should be noted that in this latter study, no BaP was added to the ambient particles.

In contrast, the relatively recent studies of Van Vaeck and Van Cauwenberghe (1984), Lindskog et al. (1985) and Pitts et al. (1986) all obtained data showing that BaP exhibited significant losses (typically 50%) when exposed to 50-1500 ppb of O_3 for time scales of 0.5-6 hr. Thus, Van Vaeck and Van Cauwenberghe (1984) observed that the percentage conversion of BaP in diesel exhaust particles, when exposed to 1.5 ppm of O_3 under high-volume sampling conditions, increased slightly with the exposure time, from 62% at 0.5 hr to 87% at 4 hr. Lindskog et al. (1985) observed conversions of BaP, on soot generated in a smoke generator, at 6 hr exposure times [45% relative humidity (RH)] increasing from 3% at 0.1 ppm O_3 to 80% at 1.0 ppm O_3. Pitts et al. (1986) observed an approximately 50% conversion of BaP, independent of the O_3 concentration (0.05-0.29 ppm O_3 at 1% RH) and of the humidity (1-50% RH at 0.20 ppm O_3), for a 3 hr exposure time. In the study of Pitts et al. (1986), BaP was either adsorbed on filters or present in particles collected close to a freeway, and the exposures were both passive (in a chamber) and in a flow system. Another recent study found degradation of BaP on ambient particles enriched with BaP and exposed to 0.18 ppm O_3, but no degradation on ambient particles sampled with an O_3 enriched (0.18 ppm) vapor stream (Coutant et al., 1988).

These data are generally consistent with the fact that BaP reacts with O_3, providing that the BaP is available for reaction. This is suggested by the often initially rapid BaP degradation followed by significantly slower BaP losses (Pitts et al., 1986; Coutant et al., 1988). Those experiments in which BaP was coated or deposited onto surfaces should then exhibit reactive losses of BaP, as generally observed (Katz et al., 1979; Peters and Seifert, 1980; Pitts et al., 1980, 1986). Fresh diesel particles (Van Vaeck and Van Cauwenberghe, 1984) and ambient particles collected near a freeway (Pitts et al., 1986) also showed BaP losses upon exposure to O_3. In contrast, BaP included in particles, as

may be expected to be the case for aged particulate matter or particles to which condensation of secondary aerosol has occurred (expected to be the case in urban atmospheres), will not be available for reaction with gaseous ozone and hence under these conditions BaP will be observed to be nonreactive (Brorström et al., 1983; Coutant et al., 1988).

Other PAH. The general conclusions drawn above concerning the reactions of BaP with ozone are also expected to apply for the other PAH, and this is supported by the available experimental data (see, for example, Brorström et al., 1983; Grosjean et al., 1983; Van Vaeck and Van Cauwenberghe, 1984; Lindskog et al., 1985; Pitts et al., 1986; Coutant et al., 1988; Greenberg, 1989). Thus, PAH included in particles will be essentially non-reactive, while those present on the particle surfaces will react with O_3, consistent with their reactivities toward O_3. The PAH which may be expected to be more reactive than BaP toward O_3 include the linear PAH (not generally very abundant in diesel exhaust) and the group of PAH containing an unsaturated cyclopenta-fused ring [i.e., with an extracyclic olefinic linkage] (Greenberg, 1989). Apart from the PAH with unsaturated cyclopenta-fused rings [as noted above, acenaphthylene, a gas-phase PAH with an unsaturated cyclopenta-fused ring, reacts in the gas-phase with O_3 (Atkinson and Aschmann, 1988)], the reactivities of the PAH toward electrophilic reaction with O_3 are expected to follow Nielsen's reactivity scale (Table 13).

2. Reaction with Oxides of Nitrogen

Benzo[a]pyrene. A number of studies have been carried out to investigate the reaction of BaP when BaP-associated particles are exposed to oxides and oxyacids of nitrogen (Pitts et al., 1978, 1985; Jäger and Hanus, 1980; Butler and Crossley, 1981; Grosjean et al., 1983; Brorström et al., 1983; Ramdahl et al., 1984; Yokley et al., 1985; Lindskog et al., 1985; Brorström-Lunden and Lindskog, 1985; Kamens et al., 1986; Arey et al., 1988). Although all of these studies observed losses of BaP and, generally, formation of nitro-BaP upon exposure of BaP-containing particles to NO_2 and/or HNO_3, the data reported are conflicting as to whether NO_2 or HNO_3 is the reactive species. In recent studies in which HNO_3 was removed from the NO_2 exposure gas, no reaction of adsorbed BaP with NO_2 was observed (Grosjean et al., 1983; Yokley et al., 1985). In contrast, Lindskog et al. (1985) did not detect any reaction of BaP on

soot with HONO or HNO_3, but did observe reaction with NO_2 and NO_2 + HNO_3 mixtures. In this latter study, the buffering effect of the soot may have played a role, and oxy- rather that nitro-PAH derivatives were generally observed as products.

Other PAH. Recent studies of pyrene in methylene chloride solution did not result in nitration when HNO_3 was present, but resulted in the formation of dinitropyrenes when N_2O_4 was present (Ross et al., 1987). These recent results of Ross and coworkers (1987) suggest that the role of HNO_3 in the nitration of PAH adsorbed on diesel soot may be to react with the soot, leading to deactivation of the soot surface and thus allowing the limited amount of NO_2/N_2O_4 to nitrate the PAH. Whether under ambient conditions HNO_3 alone can react to nitrate PAH adsorbed on diesel soot remains in question. These PAH reactions are substrate dependent (Jäger and Hanus, 1980; Ramdahl et al., 1984; Yokley et al., 1985) and, as noted above for the O_3 reactions, presumably require that the PAH be accessible for reaction.

A number of studies have been carried out in which several PAH, in addition to BaP, were examined (Butler and Crossley, 1981; Tokiwa et al., 1981; Brorström et al., 1983; Ramdahl et al., 1984; Lindskog et al., 1985; Pitts et al., 1985c). In these studies in which several PAH were examined, the nitro-PAH formed were the isomers expected from electrophilic nitration and the amounts of reaction followed the reactivity ranking of the PAH toward electrophilic nitration (Nielsen, 1984; Table 13). An apparent exception is a tentative identification of 2-nitropyrene, in addition to 1-nitropyrene, from exposure of pyrene adsorbed on silica gel to NO_2 in N_2 in the presence of light (Wu and Niki, 1985).

In ambient air, NO_2 and HNO_3 will both be present. Recently, Arey et al. (1988) studied the disappearance of perdeuterated fluoranthene, pyrene, BaP, and perylene adsorbed onto ambient particles, and the formation of the perdeuterated nitro-PAH under high-volume sampling conditions during a wintertime high-NO_x (maximum NO_x concentrations approximately 1 ppm) pollution episode in the Los Angeles air basin. BaP-d_{12} losses of ~40% were observed during the daylight sampling period on one of the two days, possibly mainly due to O_3 reaction. In contrast, no obvious overall losses of the perdeuterated fluoranthene or pyrene occurred, although

these PAH volatilized from the filters onto the downstream polyurethane foam (PUF) plugs. The data for perylene-d_{12} loss was inconclusive.

The nitro-PAH isomers formed during the ambient air sampling were perdeuterated 3-nitroperylene, 6-nitroBaP, and 1-nitropyrene. The amounts formed followed the ranking expected from the reactivity of the parent PAH toward electrophilic nitration. The maximum nitro-PAH yield was 0.1% of 3-nitroperylene-d_{11} and it was estimated that the 1-nitropyrene artifact, i.e., the amount formed during sample collection, was only ~0.1% of the 1-nitropyrene present on the particles. Thus, the formation of nitro-PAH under ambient conditions is likely to be unimportant, especially if most of the ambient particle-adsorbed PAH are unavailable for reaction.

3. Photolysis

Numerous studies have been carried out to investigate the photolysis and photooxidation of BaP and other PAH on various surfaces (Korfmacher et al., 1980; Blau and Güsten, 1981; Behymer and Hites, 1985, 1988; Kamens et al., 1985, 1986; Yokley et al., 1986; Valerio et al., 1987). All studies employing a range of substrates have concluded that photolysis rates are highly substrate dependent (Korfmacher et al., 1980; Behymer and Hites, 1985, 1988; Yokley et al., 1986), with the darker substrates leading to lower photolysis rates, presumably due to stabilization of the PAH incorporated in the particles (Behymer and Hites, 1985, 1988; Yokley et al., 1986).

Kamens et al. (1988) observed that the PAH photolysis rates (on freshly generated wood and gasoline combustion soot) depended on the temperature and ambient water concentration, with, for example, a BaP lifetime at 293 K and ~50% relative humidity at midday of ~1 hr. In contrast, for dark fly ashes, half-lives on the order of several days were observed for BaP (Behymer and Hites, 1988). The relative reactivities of the alternant PAH followed the general reactivity ranking shown in Table 13. Specifically, Behymer and Hites (1988) found for the following PAH isomer pairs that phenanthrene is more stable than anthracene, chrysene is more stable than benz[a]anthracene, benzo[e]pyrene is more stable than BaP and benzo[ghi]perylene is more stable than the linear PAH anthanthrene. Once again it can be concluded that PAH are reactive, and thus may be expected to photolyze in ambient atmospheres, but the extent to which this occurs will depend on the exact nature of the adsorbed state.

Cope and Kalkwarf (1987) and Kamens et al. (1989) have investigated the photooxidation of certain adsorbed oxygenated PAH and have found these to be generally stable to sunlight, but to decay under the influence of light and O_3.

4. Ambient Air Data

Further information concerning the atmospheric reactions and lifetimes of PAH arises from ambient air data. Arey et al. (1988) have shown that under wintertime high-NO_x conditions in southern California (with mid-day temperatures attaining 95 °F) losses of BaP-d_{12} during 12-hr sampling periods were ≤40%, and nitration of BaP-d_{12} was of negligible importance. Losses of particle-incorporated BaP would, presumably, have been lower. From an analysis of ambient air and combustion emissions data, Schuetzle and Frazier (1986) found that the benzo[e]ppyrene/benzo-[a]pyrene ratio (BeP/BaP) in ambient air of ~1.8 was very similar to the ratio observed in emission sources. Since BaP is much more reactive than BeP toward electrophilic reaction (Nielsen, 1984), reaction with O_3 (Van Vaeck and Van Cauwenberghe, 1984) and photolysis (Behymer and Hites, 1988), this observation suggests that once the BaP and BeP are adsorbed on particles they do not undergo significant degradation in the atmosphere.

Nielsen (1988) investigated the dependence of the BaP/BeP and cyclopenta[cd]pyrene/chrysene + triphenylene ratios on the wind direction, and hence the vicinity of the source, in Denmark. Higher PAH concentrations were associated with local sources, and the BaP/BeP and cyclopenta[cd]-pyrene/chrysene + triphenylene ratios were found to correlate with the BeP and chrysene + triphenylene concentrations, respectively, suggesting that BaP and cyclopenta[cd]pyrene were being degraded in the atmosphere. The author concluded that the decay rates of these two PAH were relatively fast (Nielsen, 1988). From ambient winter and summer measurements in New Jersey, Greenberg (1989) confirmed the findings of Nielsen that BaP and, especially, cyclopenta[cd]pyrene are reactive under atmospheric conditions.

Atkinson et al. (1988) measured PAH and PAH-derivatives at seven sites throughout California. Consistent with the work of Nielsen, the sites with the highest BaP/BeP ratios, Mammoth Lakes (BaP/BeP = 1.5) and Concord (BaP/BeP = 1.3), also had the highest BeP concentrations. Furthermore the BaP/BeP ratio was lowest at Glendora (BaP/BeP = 0.35) a

site where significant atmospheric reaction had occurred, as evidenced by the formation of 2-nitropyrene from pyrene (Atkinson et al., 1988). (For a complete discussion of the PAH transformations in the atmospheres sampled see Section X of Atkinson et al., 1988.) The apparent inconsistency in the data of Schuetzle and Frazier (1986) and that of Nielsen (1988) and Atkinson et al. (1988) probably reflects differences due to comparisons of averaged values from generally aged emissions (Schuetzle and Frazier, 1986) versus BaP concentrations resulting from a single emission source (such as wood smoke at Mammoth Lakes) and/or fresh emissions (Nielsen, 1988; Atkinson et al., 1988).

F. Atmospheric Formation Processes

There are no atmospheric formation pathways for PAH. PAH are present in essentially all combustion systems and sources of the PAH present in ambient air will include, in addition to diesel exhaust, emissions from gasoline-fueled automobiles, industrial processes, domestic heating systems, waste incineration facilities, tobacco smoking, agricultural burns and several natural sources, including forest fires and volcanic eruptions (Nikolaou et al., 1984).

In contrast to the PAH, nitro-PAH and other PAH derivatives (including hydroxy-PAH) are formed in the atmosphere from the gas- and adsorbed-phase reactions of the parent PAH, as well as being directly emitted from combustion sources. As discussed in Section D, the reactions of the gas-phase PAH appear to dominate in the formation of nitro-PAH (and other PAH derivatives) in the atmosphere. In ambient air studies conducted in California, the majority of the nitro-PAH observed are formed from the gas-phase atmospheric reactions of the parent PAH (Arey et al., 1987, 1989a, 1990a; Atkinson et al., 1988; Zielinska et al., 1989b). It should be noted that a large fraction of the atmospheric transformation products of the gas-phase PAH remain unidentified.

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