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JUNE 1993

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# Lifetimes and Fates of Toxic Air Contaminants in California's Atmosphere, June 1993

CALIFORNIA ENVIRONMENTAL PROTECTION AGENCY



AIR RESOURCES BOARD  
Research Division



**LIFETIMES AND FATES OF TOXIC AIR CONTAMINANTS IN  
CALIFORNIA'S ATMOSPHERE, JUNE 1993**

**Final Report  
Contract No. A032-055**

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## GLOSSARY OF TERMS, ABBREVIATIONS AND SYMBOLS

ARB	Air Resources Board
cm	Centimeter
GC	Gas chromatograph, gas chromatography, or gas chromatographic
GC-FID	Gas chromatography with flame ionization detection
HPLC	High performance liquid chromatography or high performance liquid chromatographic
i.d.	Internal diameter
in	Inch
k	Rate constant
K	Degrees Kelvin
m	Meter
M	Third body
mm	Millimeter ( $10^{-3}$ m)
m <sup>3</sup>	Cubic meter
min	Minute
m.w.	Molecular weight
NO	Nitric oxide
NO <sub>2</sub>	Nitrogen Dioxide
NO <sub>x</sub>	Oxides of nitrogen
O <sub>3</sub>	Ozone
OEHHA	Office of Environmental Health Hazard Assessment
SAPRC	Statewide Air Pollution Research Center
s	Second



## I. PROJECT SUMMARY

There is now a general awareness that the chemical compounds present in the atmosphere may pose problems to human health through exposure to them in the air we breathe, and in 1984 the California Legislature enacted AB 1807 to mandate the identification and control of toxic air contaminants in California. California's air toxics program is a two-step process which involves the identification of a toxic air contaminant, followed by the implementation of any necessary and appropriate control measures. An important element of the Air Resource Board's exposure assessment for potential toxic air contaminants concerns the atmospheric behavior of chemicals emitted into the troposphere. Specifically, for a given chemical it is necessary to have quantitative information concerning the nature and rate of its removal from the atmosphere and, if these removal processes are chemical, the products formed from these atmospheric reactions. Furthermore, since a number of potential toxic air contaminants are formed *in situ* in the atmosphere, a knowledge of these formation pathways together with an assessment of the relative balance between direct emission and *in situ* atmospheric formation is necessary. To provide the necessary information concerning the atmospheric chemistry and ambient concentrations of a series of potential toxic air contaminants, the following research tasks were conducted during this program.

### A. Literature Review of the Atmospheric Chemistry of Potential Toxic Air Contaminants

Literature reviews of the atmospheric chemistry of three potential toxic air contaminants was carried out (one of which was a class of related chemicals), and the reviews submitted to the ARB for use in its exposure documents. The chemical compounds whose atmospheric chemistry were reviewed were chosen by the ARB staff based on their priority list. The chemicals (or group of chemicals) which were dealt with in this program were:

- Di(2-ethylhexyl)phthalate
- N-Nitrosomorpholine
- Dialkylnitrosamines

For each chemical, or group of chemicals, the available literature data concerning the potentially important tropospheric removal processes were evaluated. Since chemical compounds emitted into the troposphere can be present solely in the gas phase, solely in the particle phase, or be distributed between the gas- and particle-phases, the phase distribution and the physical and chemical removal processes were considered.

In addition to these specific chemicals (or class of chemicals), the atmospheric lifetimes of a series of potential toxic air chemicals and the possible *in situ* atmospheric formation of toxic compounds were dealt with in report format.

B. Investigation of the Mutagenicity of HPLC-Separated Products of the Simulated Atmospheric Reactions of Gasoline and Terpenes

Using a microsuspension modification to the standard plate incorporation assay in conjunction with HPLC separation of extracts of collected reaction samples (Arey et al., 1992), we have investigated the formation of mutagenic products of low-volatility from the simulated atmospheric reactions of vaporized gasolines, designed to mimic the emissions from gasoline-fueled vehicles, and of a synthetic mixture of terpenes designed to simulate hydrocarbon emissions from vegetation. The data obtained showed insignificant formation of mutagenic compounds over those formed in control experiments in the absence of the vaporized gasolines or a mixture of terpenes (Table 1) and indicate that, with the sample collection and bioassay methods used, these anthropogenic and biogenic emissions are not the major sources of mutagenic compounds observed in both the gas- and particle-phase in the atmosphere in southern California (Harger et al., 1992).

Table 1. Mutagenic activities of the products of the gas-phase reactions of volatilized gasolines and a synthetic terpene mixture, together with the mutagenic activities of the HPLC blanks and chamber blanks. Tests were conducted on TA98 without S9 in the microsuspension assay. Mutagenic activities for an irradiated CH<sub>3</sub>ONO-NO-naphthalene-air mixture (Arey et al., 1992) are given for comparison.

HPLC Fraction	HPLC Column Blank			Chamber Blank			Gasoline		Terpenes	Naphthalene
	1	2	3	1	2	3	1	2		
1	0	11	0	0	0	28	0	0	0	0
2	0	17	0	0	0	0	0	0	0	0
3	0	16	20	39	0	0	0	0	0	0
4	9	10	0	85	0	0	240	300	0	72000
5	1	15	0	140	84	0	250	0	0	5200
6	22	19	0	88	72	0	0	0	0	730
7	27	35	50	0	230	0	0	0	0	11000
8	15	0	14	0	70	0	0	57	69	6200
9	14	19	62	0	35	26	0	0	0	1500
Sum	88	142	146	352	491	54	490	357	69	96630



## II. INTRODUCTION

As a result of human activities in a society as economically advanced as that in California, a spectrum of chemicals are emitted into the atmosphere from sources as diverse as fossil-fuel combustion (gasoline and diesel-fueled vehicles, residential wood combustion and heating oil combustion), industrial plants (refineries, chemical manufacturing), solvent usage, agricultural practises (pesticide use and storage, agricultural burning) and landfills and other waste disposal facilities. These chemical compounds emitted into the atmosphere are present in the atmosphere in the gas or particle phases or are distributed between the gas and particle phases. Once in the atmosphere in either the gas- or particle-phases, these chemicals are transported by the prevailing winds, and during this transport they experience physical removal processes and/or chemical reactions leading to the formation in the atmosphere of transformation products.

There is now a general awareness that the chemical compounds present in the atmosphere may pose problems to human health through exposure to them in the air we breathe (in addition to the long-term problems associated with depletion of the stratospheric ozone layer and contribution to global warming caused by the emission into the atmosphere of certain long-lived chemicals). Airborne toxic substances can cause both immediate and long-term effects. For example, sudden accidental releases of toxic air contaminants (an air pollutant which may pose a present or potential hazard to human health) can create immediate and serious health effects, and these kind of incidents are addressed through the Office of Emergency Services. Determination of the long-term health effects which occur from exposure to toxic air contaminants is the responsibility of the Air Resources Board (ARB) and the Office of Environmental Health Hazard Assessment (OEHHA). As a result of the concern over exposure to and effects from potential toxic air contaminants, in 1984 the California Legislature enacted AB 1807 to mandate the identification and control of toxic air contaminants in California.

California's air toxics program is a two-step process which involves the identification of a toxic air contaminant, followed by the implementation of any necessary and appropriate control measures. The identification phase of a toxic air contaminant involves a parallel

effort by the ARB and the OEHHA, with the OEHHA preparing a health evaluation and the ARB providing an exposure assessment. The exposure assessment prepared by the ARB includes information concerning the chemical's usage, emissions (or potential emissions), lifetime and fate in the atmosphere, ambient concentrations, and present (or potential) public exposure. These evaluations and assessments from the ARB and OEHHA form the document which is the basis for determining whether or not a chemical compound is listed as a toxic air contaminant in California. If a chemical is identified as a toxic air contaminant, then the process proceeds to the second step involving the setting and implementation of appropriate control measures.

An important element of the ARBs exposure assessment for potential toxic air contaminants concerns the atmospheric behavior of chemicals emitted into the troposphere. Specifically, for a given chemical it is necessary to have quantitative information concerning the nature and rate of its removal from the atmosphere and, if these removal processes are chemical, the products formed from these atmospheric reactions. Furthermore, since a number of potential toxic air contaminants are formed *in situ* in the atmosphere, a knowledge of these formation pathways together with an assessment of the relative balance between direct emission and *in situ* atmospheric formation is necessary. To provide the necessary information concerning the atmospheric chemistry and ambient concentrations of a series of potential toxic air contaminants, the Statewide Air Pollution Research Center (SAPRC) conducted the following specific research tasks:

- Reviewed the available literature data concerning the atmospheric chemistry and ambient concentrations of three specific chemical compounds (or group of compounds) which were in the process of review by the ARB as potential toxic air toxics, and submitted a report to the ARB for each chemical (or group of chemicals).
- Reviewed the available literature data concerning the lifetimes in the atmosphere of 23 compounds selected from the AB 2588 list of compounds and the *in situ* atmospheric formation of potential Toxic Air Pollutants from directly-emitted chemicals.

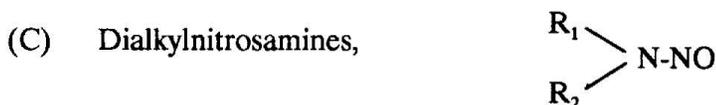
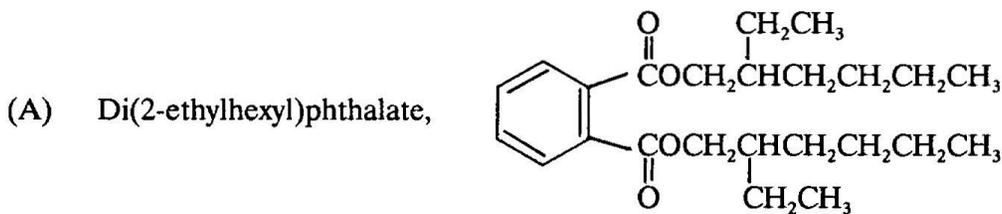
- Investigated the mutagenicity of HPLC-separated products of the simulated atmospheric reactions of vaporized gasoline and a synthetic mixture of terpenes, designed to simulate the major emissions from anthropogenic and biogenic sources, respectively.

These three specific research tasks are dealt with in Sections III and IV, below.



### III. LITERATURE REVIEW OF THE ATMOSPHERIC CHEMISTRY OF POTENTIAL TOXIC AIR CONTAMINANTS

A literature review of the atmospheric chemistry of each of three potential toxic air contaminants, or classes of compounds, was carried out, and the review submitted to the ARB for use in its exposure document. The chemical compounds whose atmospheric chemistry were reviewed were chosen by the ARB staff based on their priority list. The three chemicals (or group of chemicals) which were dealt with in this program were:



For each chemical, or group of chemicals, the available literature data concerning the following potentially important tropospheric removal processes were evaluated. Since chemical compounds emitted into the troposphere can be present solely in the gas phase, solely in the particle phase, or be distributed between the gas- and particle-phases, the phase distribution and the physical and chemical removal processes had to be considered. For compounds present in the atmosphere solely in the gas phase, the following removal processes were considered:

---

### Physical Processes

- Wet deposition.
- Dry deposition.

### Chemical Processes

- Photolysis
- Reaction with the hydroxyl (OH) radical.
- Reaction with the nitrate (NO<sub>3</sub>) radical.
- Reaction with ozone (O<sub>3</sub>).

For compounds present solely in the particle-phase, the physical removal processes of wet and dry deposition of the particles were considered, together with the possible chemical reactions of the adsorbed compounds. Of course, for chemical compounds which were distributed between the gas-and particle-phases, the complete suite of removal processes were considered. In addition to reviewing the literature data concerning the rates of these various removal processes, the available literature data dealing with the chemical transformation products of these reactions were reviewed.

The general format of these reports was as follows:

- Introduction
- Phase Distribution in the Atmosphere
- Chemical Loss Processes
  - Reaction with Ozone
  - Reaction with the Hydroxyl Radical
  - Reaction with the Nitrate Radical
  - Photolysis
- Physical Loss Processes
- Tropospheric Lifetime and Fate
- Atmospheric Formation
- Conclusions
- References

The reviews as submitted to the ARB (with the references updated, wherever possible, but with no other changes) are given in Appendices D, E and F, respectively.

In addition to these three reports dealing with specific compounds or classes of compounds, more general reports were submitted to the ARB dealing with:

- The estimated atmospheric lifetimes of 23 organic compounds selected from the AB 2588 list of chemicals for which "monitoring data must be obtained."
- The formation in the atmosphere of potential Toxic Air Pollutants.
- As a specific example of the atmospheric formation of potential Toxic Air Pollutants, the routes for formation of acrolein ( $\text{CH}_2=\text{CHCHO}$ ) in the atmosphere.

These three reports, as submitted to the ARB (with the references updated, wherever possible, but with no other changes) are given in Appendices A, B, and C, respectively. In addition to these six reports submitted to the ARB and given in Appendices A through F, Dr. Roger Atkinson prepared, under partial support from this ARB program, a critical review and evaluation of the gas-phase chemistry of organic compounds, entitled "Gas-Phase Tropospheric Chemistry of Organic Compounds," which will be published by the *Journal of Physical and Chemical Reference Data* as a Monograph. The title page and list of contents of this in-press monograph are attached as Appendix G.



#### IV. INVESTIGATION OF THE MUTAGENICITY OF HPLC-SEPARATED PRODUCTS OF THE SIMULATED ATMOSPHERIC REACTIONS OF GASOLINE AND TERPENES

##### A. Introduction

There is abundant evidence that extracts of ambient particles of respirable size range collected in polluted atmospheres are mutagenic (see, for example, Pitts et al., 1977, 1982; Tokiwa et al., 1977; Talcott and Wei, 1977; Siak et al., 1985; de Raat et al., 1985; de Raat and de Meijere, 1988; Arey et al., 1988, 1992; Atkinson et al., 1988; Lewtas et al., 1990) and carcinogenic (Leiter et al., 1942). However, to date there have been very few reported studies concerning the mutagenicity of ambient air gas-phase samples (de Raat et al., 1987; Wong et al., 1991; Harger et al., 1992), possibly in part because of the reported presence of mutagenic artifacts from the sampling media (de Raat et al., 1987).

There have been, however, a number of studies conducted by Kleindienst and Shepson and coworkers (Shepson et al., 1985a,b, 1987; Kleindienst et al., 1985a,b, 1986, 1990, 1992a,b; Dumdei et al., 1988) in which the mutagenicities of gas-phase peroxyacyl nitrates and of the gas-and particle-phase products from NO<sub>x</sub>-air irradiations of volatile organic compounds and mixtures have been investigated. In these studies, the gas-phase mutagenicities were studied by exposing, in a flow-through mode, *Salmonella typhimurium* in agar in glass Petri dishes to the effluent of an environmental chamber operated in dynamic mode. The production of mutagenic gas-phase products were detected using strain TA100 from the NO<sub>x</sub>-air irradiations of toluene (Shepson et al., 1985a; Dumdei et al., 1988; Kleindienst et al., 1992a), propene (Kleindienst et al., 1985a, 1992a), allyl chloride (Shepson et al., 1987) and n-butane (Kleindienst et al., 1992a), with the relative activities being in the order allyl chloride > toluene > propene > n-butane (Kleindienst et al., 1992a). The compound(s) responsible for the observed mutagenic activities have not been determined, although the peroxyacyl nitrates, including peroxyacetyl nitrate (PAN), were shown to be mutagenic towards strain TA100 (Kleindienst et al., 1985b, 1990). Kleindienst et al. (1986, 1992b) also showed that the products of irradiated NO<sub>x</sub>-wood smoke-air and NO<sub>x</sub>-automobile emissions-air mixtures were mutagenic towards strains TA98 and TA100, and that the gas-

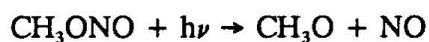
phase mutagenicities (in terms of revertants  $m^{-3}$ ) were greater than the particle-phase mutagenicities.

Recently, we have used HPLC to separate extracts of samples prior to conducting the mutagenicity tests on Ames strain TA98 in the absence of metabolic activation (Arey et al., 1992; Harger et al., 1992). Samples collected from ambient air on glass fiber filters (particle-phase) and polyurethane foam (PUF) plugs (semi-volatile vapor-phase), as well as from air samples collected from environmental chamber experiments, have been tested with this separation followed by bioassay approach. We observed that the vapor-phase and particle-phase mutagenicities were of similar magnitude for samples collected at a site in Southern California (Harger et al., 1992). Furthermore, our data showed that with this microsuspension modification of the standard plate incorporation assay and using strain TA98, the vapor-phase mutagenicity was found largely in the nitroarene-containing HPLC fraction, while the particle-phase mutagenicity was mainly due to 2-nitrodibenzopyranone (Harger et al., 1992; Helmig et al., 1992a,b).

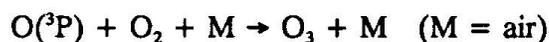
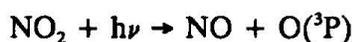
Ambient air data in the Los Angeles air basin and elsewhere show that to a good approximation the composition of ambient air volatile organic compounds is very similar to that of gasoline fuel (Harley et al., 1992). For example, gasoline fuel is comprised of ~55-65% alkanes, ~5-10% alkenes and ~25-35% aromatic hydrocarbons (Lonneman et al., 1986; Sigsby et al., 1987; Harley et al., 1992), while the ambient air composition in the Los Angeles area is ~50-55% alkanes, ~5-15% alkenes, ~25-30% aromatic hydrocarbons and ~5-15% carbonyl compounds (Grosjean and Fung, 1984; ARB, 1992). A further source of ambient air VOCs is the emission of non-methane biogenic organics, including isoprene, monoterpenes and sesquiterpenes (Rasmussen, 1972; Isidorov et al., 1985; Lamb et al., 1987; Arey et al., 1991a,b; Winer et al., 1992). In this work, we have conducted simulated atmospheric photooxidations of vaporized gasoline fuel and a synthetic mixture of terpenes in order to assess the importance of these VOCs as precursors of the measured direct-acting mutagenicity of ambient air.

## B. Experimental

The experimental methods were generally similar to those described by Arey et al. (1992) and Harger et al., (1992). The photooxidation experiments were carried out in a 6400 liter all-Teflon chamber (Figure 1), with irradiation provided by two parallel banks of Sylvania F40/350BL blacklamps (40 lamps per bank), leading to an NO<sub>2</sub> photolysis rate of 0.45 min<sup>-1</sup> at the maximum light intensity (which is similar to the outdoor NO<sub>2</sub> photolysis rate for overhead sun conditions). In order to simulate atmospheric photooxidation conditions on a short time-scale, hydroxyl (OH) radicals were generated from the photolysis of methyl nitrite (CH<sub>3</sub>ONO) in air at wavelengths >300 nm



The initial CH<sub>3</sub>ONO and NO mixing ratios in the reactant mixtures were 2 parts-per million (ppm) and 1 ppm, respectively. These initial reactant concentrations led to sufficient NO to NO<sub>2</sub> conversion that O<sub>3</sub> and NO<sub>3</sub> radicals were generated during the experiments (see Atkinson et al., 1989)



Hence the organic compounds in the chamber were exposed to OH radicals, NO<sub>3</sub> radicals and O<sub>3</sub>, as is the case in the ambient atmosphere (Atkinson, 1988).

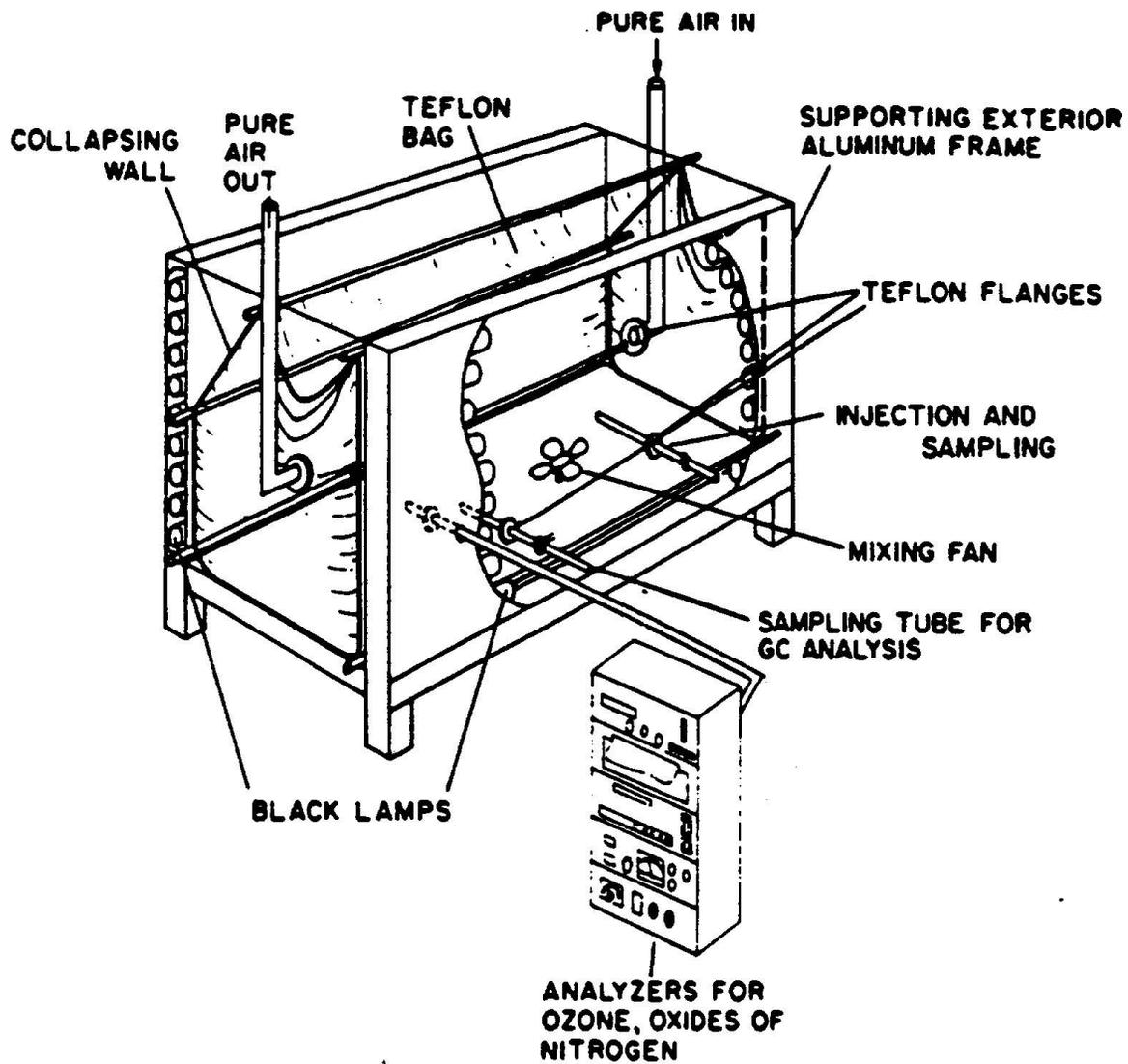


Figure 1. Schematic of SAPRC 6400-liter all-Teflon chamber.

In the experiments with vaporized gasoline, 50  $\mu\text{l}$  of gasoline (either Unocal unleaded, 87 octane, or Arco EC-1 reformulated gasoline) were added to the chamber together with the methyl nitrite and NO and irradiated for 10 mins at the maximum light intensity (50  $\mu\text{l}$  of gasoline is equivalent to  $\sim 9$  ppmC in the 6400 liter chamber). For the experiments to investigate the mutagenicity of the atmospheric photooxidations of biogenic emissions, 40  $\mu\text{l}$  of a mixture (5  $\mu\text{l}$  each) of isoprene, the monoterpenes  $\alpha$ -pinene,  $\beta$ -pinene, sabinene, limonene and ocimene, and the sesquiterpenes  $\alpha$ -humulene and  $\beta$ -caryophyllene were irradiated in the presence of  $\text{CH}_3\text{ONO}$  and NO for 10 mins at the maximum light intensity. These conditions were similar to those used for our previous mutagenicity studies of the products of the gas-phase atmospheric reactions of naphthalene and phenanthrene (Arey et al., 1992). Control experiments were carried out in which  $\text{CH}_3\text{ONO}$ -NO-air mixtures were irradiated under identical conditions of initial  $\text{CH}_3\text{ONO}$  and NO mixing ratios and irradiation intensity and duration.

Large volume samples ( $\sim 3000$  liter total volume sampled) were collected onto polyurethane foam (PUF) plugs (four 0.5 min samples, each collected onto a single PUF plug), which were then solvent extracted and HPLC-fractionated as described by Arey et al. (1992). The PUF plugs were Soxhlet extracted with  $\text{CH}_2\text{Cl}_2$  for 4 hrs. The dichloromethane extracts of the PUF plugs were filtered through 0.45  $\mu\text{m}$  Acrodisc Teflon filters, and fractionated by normal-phase HPLC using a semipreparative Regis Spherisorb SSW silica column, 25 cm x 10 mm. The HPLC instrumentation consisted of a Spectra-Physics Model 8100 gradient liquid chromatograph with a Model 8400 UV/VIS detector ( $\lambda = 254$  nm) and an ISCO fraction collector. The solvent program (at a flow rate of 3 ml  $\text{min}^{-1}$ ) was: initially 100% hexane for 10 mins, followed by a 5-min linear gradient to 95% hexane and 5%  $\text{CH}_2\text{Cl}_2$ . The solvent was programmed over the next 25 min to 100%  $\text{CH}_2\text{Cl}_2$  where it was held for 10 mins, then programmed to 100% acetonitrile over 10 mins, held isocratic for 10 min and then programmed back to the initial conditions. Beginning after 1 min, 9 nine-minute fractions of increasing polarity were collected for bioassay testing.

The HPLC fractions were tested for mutagenicity using *Salmonella typhimurium* strain TA98 without exogenous (S9) activation and using the Kado microsuspension preincubation modification (Kado et al., 1983, 1986; Arey et al., 1992; Harger et al., 1992) of the histidine-

reversion bioassay of Ames and coworkers (Ames et al., 1975; Maron and Ames, 1983). The HPLC fractions were dissolved in  $\text{CH}_2\text{Cl}_2$  and solvent-exchanged into DMSO (Mallinckrodt Spectra AR grade, 5  $\mu\text{l}$ ), combined with 100  $\mu\text{l}$  ( $\sim 1.1 \times 10^{10}$  cells  $\text{ml}^{-1}$ ) aliquots of the resuspended cell culture and incubated for 90 min at 37°C with vigorous shaking (180 rpm). Following the addition of 2.0 ml of soft agar and mixing, each sample was overlaid onto minimal glucose plates which were incubated at 37°C for 63 hrs and scored by means of an automatic colony counter. The slope of the initial portion of the dose-response curve was used to calculate the mutagenic activity.

### C. Results

The mutagenicity testing of the various HPLC fractions of the PUF plug extracts of irradiated  $\text{CH}_3\text{ONO-NO-air}$ ,  $\text{CH}_3\text{ONO-NO-gasoline-air}$  and  $\text{CH}_3\text{ONO-NO-terpene-air}$  mixtures lead to a series of "mutagrams," consisting of the mutagenic activity versus HPLC fraction number, with the polarity of the compounds increasing with increasing fraction number. We also conducted mutagenicity testing of the HPLC fractions of the solvent (HPLC blank). The mutagenic activities as a function of HPLC fraction number of the HPLC blanks, irradiated  $\text{CH}_3\text{ONO-NO-air}$  (chamber blank),  $\text{CH}_3\text{ONO-NO-vaporized gasoline-air}$  and  $\text{CH}_3\text{ONO-NO-terpene-air}$  mixtures are given in Table 2. It can be seen from this table that the mutagenic activities of the irradiated mixtures containing the vaporized gasolines and the terpenes were low and little different from the  $\text{CH}_3\text{ONO-NO-air}$  chamber control mixtures. For comparison, the previous data of Arey et al. (1992) for an irradiated  $\text{CH}_3\text{ONO-NO-air}$  mixture containing the same concentrations of methyl nitrite and NO and the same irradiation times and light intensity, but with an initial naphthalene mixing ratio of 0.91 ppm (9.1 ppmC) are also given in Table 2. Clearly, the naphthalene photooxidation products collected on PUF plugs are 2-3 orders of magnitude more mutagenic (for a similar ppmC of organic reactant) than are the gasoline or terpene photooxidation products. It should however be noted that, due to their volatility, the gasoline or terpene reaction products may not have been quantitatively collected on the PUF solid adsorbent. The data obtained in these experiments shows that on an initial carbon

Table 2. Mutagenic activities of the products of the gas-phase reactions of volatilized gasolines and a synthetic terpene mixture, together with the mutagenic activities of the HPLC blanks and chamber blanks. Tests were conducted on TA98 without S9 in the microsuspension assay. Mutagenic activities for an irradiated CH<sub>3</sub>ONO-NO-naphthalene-air mixture (Arey et al., 1992) are given for comparison.

HPLC Fraction	HPLC Column Blank			Chamber Blank			Photooxidation of Gasoline		Terpenes	Naphthalene
	1	2	3	1	2	3	1	2		
1	0	11	0	0	0	28	0	0	0	0
2	0	17	0	0	0	0	0	0	0	0
3	0	16	20	39	0	0	0	0	0	0
4	9	10	0	85	0	0	240	300	0	72000
5	1	15	0	140	84	0	250	0	0	5200
6	22	19	0	88	72	0	0	0	0	730
7	27	35	50	0	230	0	0	0	0	11000
8	15	0	14	0	70	0	0	57	69	6200
9	14	19	62	0	35	26	0	0	0	1500
Sum	88	142	146	352	491	54	490	357	69	96630

basis, gasoline and terpenes generate markedly less direct-acting mutagenicity than does naphthalene, the simplest polycyclic aromatic hydrocarbon (PAH).

#### D. Discussion

In recent studies, Kleindienst et al. (1992a) have shown that the NO<sub>x</sub>-air photooxidations of representative alkanes, alkenes and aromatic hydrocarbons lead to the formation of mutagenic compounds (towards strain TA100) using their experimental method, which may well be more effective in detecting the more volatile or highly reactive gas-phase mutagens than the method employed here using PUF solid adsorbent. Using simulated automobile emissions mixtures, Kleindienst et al. (1992b) showed that the NO<sub>x</sub>-air photooxidation of this synthetic mixture designed to simulate automobile exhaust emissions plus evaporative emission leads to the formation of gas-phase mutagenicity towards both strains TA98 and TA100. While we have observed no obvious enhancement of the chamber blank mutagenicity, this may not be inconsistent with the data of Kleindienst et al. (1992b) when account is taken of the differing experimental procedures used to "collect" the mutagenic compounds; collection on PUF solid adsorbent in this work [which has low collection efficiency for the more volatile organic compounds (see Hakola et al., 1993 for collection of C<sub>7</sub>-C<sub>9</sub> carbonyls)] versus adsorption (via dry deposition) into static agar-containing plates in the study of Kleindienst et al. (1992b). It is also possible that the method of Kleindienst et al. (1992b), in which the irradiation chamber is operated as a stirred flow reactor with the *Salmonella* plates being exposed for 4-10 hours to the chamber effluent, is markedly more sensitive than our short time-scale "batch" experiments because of the exposure of the bacteria to greater quantities of reaction products. However, until single NO<sub>x</sub>-PAH-air (for example, of naphthalene) photooxidations and ambient air measurements are carried out using the experimental procedures of Kleindienst et al. (1992a,b), no realistic comparison of these two methods can be made.

Our experimental conditions were chosen to be similar to those used for our previous studies concerning the gas- and particle-phase mutagenicity of ambient air (Harger et al., 1992) and of the mutagenicity of the photooxidation products of the 2-3 ring gas-phase PAH (Arey et al., 1992; Helmig et al., 1992a). Since the OH radical concentrations in the

CH<sub>3</sub>ONO-NO-organic-air irradiations were in the range (2-3) x 10<sup>8</sup> molecule cm<sup>-3</sup>, a factor of 100-200 higher than ambient atmospheric levels (Arey et al., 1989; Prinn et al., 1992), the 10-min chamber irradiations were equivalent to photooxidation in the atmosphere for ~15-30 hrs (or 1-2 days since OH radicals are only present at significant concentrations during daylight hours). Thus, our chamber experiments were equivalent to at least a one-day atmospheric oxidation, as occurs in, for example, the Los Angeles air basin in single-day pollution episodes. Since the photolysis lifetime of CH<sub>3</sub>ONO in the 6400 liter all-Teflon chamber is ~6 min at the light intensity used in this work (S. M. Aschmann and R. Atkinson, unpublished data, 1993), continuation of irradiations beyond 10 mins duration would result in depletion of CH<sub>3</sub>ONO and hence of OH radicals and the experiments would then be largely photolysis and reaction with O<sub>3</sub> and NO<sub>3</sub> radicals.

As noted above, the PUF plugs do not collect volatile organic compounds. However, in most cases we expect that volatile organic compounds are not mutagenic (or are not strongly mutagenic) and hence the more complex, less volatile, organic compounds which may exhibit mutagenic activity are probably collected with some degree of efficiency by the PUF collection medium. For example, comparison of Tables 3 and 4 shows that the non-mutagenic (TA98, -S9) nitroaromatic compounds (Table 3) are generally of lower molecular weight (M.W.) than are the mutagenic nitroaromatic compounds listed in Table 4. The mutagenic activities of these nitroaromatic compounds were determined at SAPRC using the microsuspension modification of the Ames bioassay.

The estimated emissions of non-methane biogenic organic compounds into the Los Angeles basin are ~100-150 tons per day, a factor of ~15 lower than the emissions of anthropogenic non-methane hydrocarbons (NMHC) into the Los Angeles basin. With an NMHC concentration in the Los Angeles basin of ~700 ppbC, as measured during the 1987 SCAQS (ARB, 1992), this would correspond to ~40 ppbC of biogenic non-methane organic compounds (observed ambient levels are lower, due in part to the much higher reactivities of the terpenes compared to anthropogenic NMHC). We measured a naphthalene concentration of 7 ppbC at Glendora during the Carbonaceous Species Intercomparison Study in 1986 (Arey et al., 1989). Thus, based on our previous chamber data for

Table 3. Nitroaromatic compounds which are not directly mutagenic to TA98 in the microsuspension preincubation test.

Compound	M. W.
Nitrobenzene	123
o-Nitrotoluene	137
m-Nitrotoluene	137
p-Nitrotoluene	137
o-Nitrophenol	139
m-Nitrophenol	139
2-Methyl-3-nitrophenol	153
2-Methyl-4-nitrophenol	153
2-Methyl-6-nitrophenol	153
3-Methyl-2-nitrophenol	153
3-Methyl-4-nitrophenol	153
5-Methyl-2-nitrophenol	153

Table 4. Nitroaromatic compounds which are directly mutagenic to TA98 in the microsuspension preincubation test.

Compound	M. W.	Mutagenicity rev nmol <sup>-1</sup>
p-Nitrophenol	139	0.57
1-Nitronaphthalene	173	48 <sup>a</sup>
2-Nitronaphthalene	173	890 <sup>a</sup>
3-Nitrobiphenyl	199	26
1-Nitrofluorene	211	860 <sup>a</sup>
2-Nitrofluorene	211	4,100 <sup>a</sup>
3-Nitrofluorene	211	5,500 <sup>a</sup>
4-Nitrofluorene	211	34 <sup>a</sup>
2-Nitro-6H-dibenzo[bd]pyran-6-one	241	58,600 <sup>a</sup>
3-Nitro-6H-dibenzo[bd]pyran-6-one	241	10,000
4-Nitro-6H-dibenzo[bd]pyran-6-one	241	480 <sup>a</sup>
8-Nitro-6H-dibenzo[bd]pyran-6-one	241	6,500

<sup>a</sup>From Arey et al. (1992).

naphthalene (Arey et al., 1992) and the present data for vaporized gasoline and terpenes, the contribution of naphthalene reaction products [chiefly 2- and 1-nitronaphthalene (Atkinson et al., 1987; Arey et al., 1992)] to the direct-acting TA98 mutagenicity of an ambient air sample collected on PUF solid adsorbent in the Los Angeles basin would dominate over the contributions of gasoline vapor and terpene photooxidation products. Indeed, the direct-acting mutagenicity of the terpene photooxidation products collected on PUF plugs is calculated to be of negligible or minor importance. It must, however, be remembered that these results are for a single assay system, TA98 (-S9), and the results could certainly differ if another bioassay system was used. It should also be noted that highly reactive compounds such as the terpenes may photooxidize to form short-lived mutagens such as epoxides which would not survive sample collection and workup using current technology.

Based on the ambient HPLC fractionated gas- and particle-phase mutagenicity measured by Harger et al. (1992) and the contribution of nitronaphthalenes to this gas-phase mutagenicity, 2-nitronaphthalene appears to account for ~3-4% of the total PUF + filter mutagenicity for the Claremont, CA, sample. Furthermore, the data of Arey et al. (1992) show that 2-nitronaphthalene accounts for ~50% of the total mutagenicity of the PUF-collected reaction sample from naphthalene photooxidation. This then implies that the naphthalene photooxidation reaction products account for ~7% of the total PUF + filter mutagenicity in the ambient sample collected in southern California, using our collection, fractionation and mutagenicity testing procedures.

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## **APPENDICES**



# APPENDIX A

## ATMOSPHERIC LIFETIMES OF POTENTIAL TOXIC AIR CONTAMINANTS

Draft Report to California Air Resources Board  
in partial fulfillment of Contract No. A032-055

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ARB-91:arbtoxics

It is now well recognized that organic compounds present in the troposphere in the gas phase are removed and/or transformed by a number of physical and chemical processes (Atkinson, 1988a; Bidleman, 1988). These are briefly discussed in the sections below.

#### Physical Removal Processes

The physical removal processes are wet and dry deposition. For gas-phase organic compounds with lifetimes in the troposphere due to chemical reaction of the order of weeks or less, dry deposition is expected to be, at most, of minor significance. Wet deposition involves the uptake of chemicals into rain, cloud and fog water, and the key parameter is the Washout Ratio,  $W$ ,

$$W = [\text{chemical}]_{\text{rain}}/[\text{chemical}]_{\text{air}}$$

where  $[\text{chemical}]_{\text{rain}}$  and  $[\text{chemical}]_{\text{air}}$  are the concentrations of the organic compound in the aqueous phase and in air, respectively. For washout, or wet deposition, of a chemical to be very efficient (i.e., for the chemical to be essentially totally removed by a rain event, for example), the washout ratio needs to be in the range  $W = 10^4$  to  $10^6$ . Since the washout ratio is related to the Henry's Law constant,  $H$ , by,

$$W = RT/H$$

chemicals which undergo efficient rainout are those which are highly soluble in the aqueous phase.

#### Chemical Transformation Processes

The potentially important chemical removal/transformation processes in the troposphere for gas-phase organic compounds are photolysis and reaction with OH and NO<sub>3</sub> radicals and O<sub>3</sub> (Atkinson, 1988a, 1990). For basic compounds such as the amines and hydrazines, gas-phase reaction with gaseous nitric acid to form the ionic salts may also be important.

In order to calculate the tropospheric lifetimes for a given organic compound with respect to reaction with the OH radical, reaction with the NO<sub>3</sub> radical, and reaction with O<sub>3</sub>, the rate constant for the particular reaction and the ambient tropospheric concentration of the reactive species (OH radical, NO<sub>3</sub> radical, or O<sub>3</sub>) must be known. For example, the lifetime of a chemical with respect to reaction with the OH radical, τ<sub>OH</sub>, is given by

$$\tau_{OH} = (k_{OH}[OH])^{-1}$$

where k<sub>OH</sub> is the rate constant for the OH radical reaction and [OH] is the ambient tropospheric OH radical concentration.

While the rate constants for the gas-phase reactions of a large number of organic compounds with OH and NO<sub>3</sub> radicals and O<sub>3</sub> are either reliably known (Atkinson and Carter, 1984; Atkinson, 1989, 1990, 1991) or can be estimated reasonably well (Atkinson, 1987, 1988b) [to possibly a factor of 2-5 (Atkinson, 1988b)], the ambient atmospheric concentrations of the OH radical and, especially, the NO<sub>3</sub> radical are highly uncertain at any particular time and place.

There are few direct measurements of the tropospheric OH radical concentration (Hübner et al., 1984; Perner et al., 1987; Platt et al., 1988), and reported daytime concentrations are the range <5 x 10<sup>5</sup> to 9 x 10<sup>6</sup> molecule cm<sup>-3</sup>. These direct measurements are in agreement with indirect measurements of lower tropospheric OH radical concentrations (Ayers and Gillett, 1988; Arey et al., 1989), and are also consistent with the global tropospheric OH radical concentration derived from the emissions and atmospheric concentrations of methylchloroform (Prinn et al., 1987). In this report, a 12-hr average OH radical concentration of 1.5 x 10<sup>6</sup> molecule cm<sup>-3</sup> (equivalent to a 24-hr average of 7.5 x 10<sup>5</sup> molecule cm<sup>-3</sup>) is used, as derived from the global tropospheric OH radical concentration (Prinn et al., 1987).

The situation is worse for the NO<sub>3</sub> radical, with measured lower tropospheric NO<sub>3</sub> radical concentrations ranging from <5 x 10<sup>7</sup> to 1 x 10<sup>10</sup> molecule cm<sup>-3</sup> (Atkinson et al., 1986). As recommended by Atkinson (1991), a 12-hr nighttime average NO<sub>3</sub> radical concentration of 5 x 10<sup>8</sup> molecule cm<sup>-3</sup> is used here, with the realization that this NO<sub>3</sub> radical

concentration is uncertain to at least an order of magnitude (Atkinson, 1991).

Ozone concentrations are routinely measured in the lower troposphere, and a 24-hr average  $O_3$  concentration of  $7 \times 10^{11}$  molecule  $cm^{-3}$  is used here, based on the review of Logan (1985) of  $O_3$  concentrations in the non-urban lower troposphere.

#### Estimated Tropospheric Lifetimes for Selected Potential Toxic Air Contaminants

In Table I, the estimated lifetimes of organic compounds selected from the California AB 2588 "Inventory of Substances for which Emissions must be Quantified" are given for reaction with OH and  $NO_3$  radicals and  $O_3$ , photolysis (where known), and physical loss processes (if expected to be important). In addition, the estimated overall lifetime is also given. The overall lifetimes (listed under the column labelled "Total" in Table I) can then be used with the estimated emissions data to qualitatively assess the doses of these chemicals to which populations will be exposed to.

Table I. Calculated Tropospheric Lifetimes for Selected Organic Compounds Present in the Gas Phase in the Troposphere.

Organic	Lifetime (days) due to Removal/Transformation Process					
	OH	NO <sub>3</sub>	O <sub>3</sub>	hν	Physical	Total
Acetamide	≥0.8	a	b	b	b	≥0.8
Acrolein	0.8	42	59	~10	b	0.7
Acrylamide	≥0.6	a	b	b	b	≥0.6
Acrylonitrile	4.5	b	b	b	b	4.5
Allyl chloride	0.9	87	11	b	b	0.8
Benzyl chloride	5.3	>80	>400	b	b	5.3
Bis(chloro- methyl)ether	4.0	b	b	b	b	4.0
Chlorobenzene	20	>15000	>1600	b	a	~20
Cresols	~0.3	~0.004	-55	b	c	<0.3
N,N-Dimethyl- nitrosamine <sup>d</sup>	6.1	a	>550	~0.003	b	0.003
1,4-Dichloro- benzene	48	>1300	>3300	b	a	48
Dimethylamine	0.2	a	6.4	b	b	0.2
1,1-Dimethyl- hydrazine	0.3	a	<0.02	b	b	<0.02
Dimethyl sulfate	>30	b	>12000	b	a	>30
1,4-Dioxane	1.4	b	b	b	b	1.4
Ethyl acrylate	>2	b	b	b	b	>2
Hexachloro- benzene	~770	b	>1600	b	a	~770
Hydrazine	0.2	a	0.6	b	b	0.2
4,4'-Methylene dianiline	~0.5	a	b	b	b	~0.5
Phenol	0.6	0.01	b	b	c	<0.6
Propylene oxide	30	b	b	b	b	30
Toluene di- isocyanates	2.2	b	b	b	b	2.2
2,4,6-Trichloro- phenol	≥15	a	b	b	c	≥15

<sup>a</sup>No data available; may be important.

<sup>b</sup>No data available; not expected to be important.

<sup>c</sup>Washout is rapid.

<sup>d</sup>While photolyzes rapidly during daylight hours, is expected to be stable during nighttime hours.

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# APPENDIX B

## ATMOSPHERIC FORMATION OF POTENTIAL TOXIC ORGANIC AIR POLLUTANTS

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## Abstract

Review of the gas-phase reactions of anthropogenically emitted alkanes, alkenes, aromatic hydrocarbons, polycyclic aromatic hydrocarbons and chloroethenes indicates that the following classes of potential toxic air contaminants are formed in the atmosphere during transport from source to receptor.

Organic Class	Examples
Aldehydes	formaldehyde (HCHO) acetaldehyde (CH <sub>3</sub> CHO)
1,2-Hydroxyaldehydes	glycolaldehyde (HOCH <sub>2</sub> CHO)
1,4-Hydroxyaldehydes	4-hydroxybutanal (HOCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CHO)
Aromatic aldehydes	benzaldehyde (C <sub>6</sub> H <sub>5</sub> CHO)
α,β-Unsaturated aldehydes	acrolein (CH <sub>2</sub> =CHCHO)
Ketones	acetone (CH <sub>3</sub> C(O)CH <sub>3</sub> ) methyl ethyl ketone (CH <sub>3</sub> C(O)CH <sub>2</sub> CH <sub>3</sub> )
1,4-Hydroxyketones	CH <sub>3</sub> C(O)CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> OH
Alkyl nitrates	2-butyl nitrate (CH <sub>3</sub> CH(ONO <sub>2</sub> )CH <sub>2</sub> CH <sub>3</sub> ) 2-pentyl nitrate (CH <sub>3</sub> CH(ONO <sub>2</sub> )CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub> ) 3-pentyl nitrate (CH <sub>3</sub> CH <sub>2</sub> CH(ONO <sub>2</sub> )CH <sub>2</sub> CH <sub>3</sub> )
1,2-Hydroxynitrates	CH <sub>3</sub> CH(OH)CH <sub>2</sub> ONO <sub>2</sub>
1,2-Carbonyl nitrates	CH <sub>3</sub> C(O)CH <sub>2</sub> ONO <sub>2</sub> CH <sub>3</sub> CH(ONO <sub>2</sub> )CHO
Phenolic compounds	phenol (C <sub>6</sub> H <sub>5</sub> OH) o-cresol (ortho-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> OH) 1,2-dihydroxybenzene (C <sub>6</sub> H <sub>4</sub> (OH) <sub>2</sub> ) 2-hydroxybiphenyl

Nitroaromatics	m-nitrotoluene nitrobenzene 3-nitrobiphenyl 2-nitrofluoranthene
Hydroxynitro-aromatics	2-nitrophenol 4-nitrophenol hydroxynitrotoluenes hydroxynitronaphthalenes
Acyl peroxy nitrates	peroxyacetyl nitrate ( $\text{CH}_3\text{C}(\text{O})\text{OONO}_2$ ) peroxypropionyl nitrate ( $\text{CH}_3\text{CH}_2\text{C}(\text{O})\text{OONO}_2$ ) peroxybenzoyl nitrate ( $\text{C}_6\text{H}_5\text{C}(\text{O})\text{OONO}_2$ )

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## INTRODUCTION

Organic compounds are emitted into the atmosphere from a number of anthropogenic sources, including gasoline- and diesel-fueled vehicle exhaust, fossil-fueled power plants, landfills, industrial processes, waste incineration facilities, and commercial and domestic heating systems (Graedel et al., 1986). While organic compounds are also emitted into the atmosphere from vegetation (Isidorov et al., 1985; Arey et al., 1991a,b,c), organic compounds of biogenic origin are not discussed in this report, although in many cases their reactions are analogous to those of structurally-related compounds of anthropogenic origin. In the atmosphere, organic compounds are distributed between the gas- and particle-phases, depending mainly on their volatility (Bidleman, 1988). From theoretical considerations together with measured ambient atmospheric gas/particle distributions for various classes of organic compounds, Bidleman (1988) concluded that the determining factor influencing the gas/particle phase distribution is the liquid-phase vapor pressure of the organic compound, with compounds with vapor pressures at ambient temperatures  $<10^{-6}$  Torr being partitioned largely into the particle phase, and those with liquid-phase vapor pressures  $>10^{-6}$  Torr existing largely in the gas phase. Ambient air data for the gas/particle phase distributions of dibenzo-p-dioxans and dibenzofurans (Eitzer and Hites, 1986, 1989a,b), polycyclic aromatic hydrocarbons (Arey et al., 1987; Coutant et al., 1988), and alkanes (Bidleman et al., 1988) support Bidleman's conclusions.

In the atmosphere, in either the gas or particle phase, organic compounds can undergo photolysis and chemical reactions leading to transformation products which may be more or less toxic than the directly emitted parent compound. The potential transformation processes and lifetimes of organic chemicals due to photolysis and/or chemical reaction depend to a large extent on the phase (gas versus particle) in which the compound exists. Our knowledge concerning gas- and particle-phase reactions of organic compounds is briefly discussed in the following sections.

### Particle-Phase Transformations of Organic Compounds

Few quantitative data on particle-phase photolysis and chemical reactions for atmospherically-realistic substrates exist and hence only qualitative statements, at best, for these transformations can be given. It is expected that the transformation processes for particle-associated organic compounds are photolysis and reaction with  $O_3$ ,  $NO_2$ ,  $HNO_3$ ,  $H_2O_2$ ,  $SO_2$ , and  $H_2SO_4$  (and possibly other species). An upper limit to the atmospheric lifetime of the particle-associated organic compounds may be taken as that of their host particles which will undergo wet and/or dry deposition. Because of the paucity of data on particle-phase reactions and transformations, this report deals only with the transformation products of gas-phase organic compounds.

### Gas-Phase Transformations of Organic Compounds

In the gas phase, organic compounds can undergo transformations by photolysis, reaction with the OH radical, reaction with the  $NO_3$  radical, and reaction with  $O_3$  (Atkinson, 1988, 1989, 1990a,b, 1991). The rate constants for these gas-phase OH radical,  $NO_3$  radical and  $O_3$  reactions have been measured for a large number of organic compounds (Atkinson and Carter, 1984; Atkinson, 1989, 1991), and estimation techniques have been developed for the calculation of rate constants for organic compounds for which experimental data do not presently exist. These kinetic data allow the atmospheric lifetimes of gas-phase organic compounds due to photolysis and reactions with OH and  $NO_3$  radicals and  $O_3$  to be estimated, as shown in Table 1 for selected organic compounds of anthropogenic origin.

The alkanes and aromatic hydrocarbons react in the atmosphere solely by daytime reaction with the OH radical. The alkenes react with OH and  $O_3$  during daylight hours, and with  $NO_3$  radicals and  $O_3$  during nighttime (Table 1). The modes of reaction of oxygenated compounds are varied. The present state of knowledge concerning the main details of the gas-phase reactions and the expected products for the major classes of organic compounds present in ambient atmospheres are dealt with here and these include: the alkanes, alkenes, aromatic hydrocarbons, polycyclic aromatic hydrocarbons (PAH), and the simple chloroethenes (for example, trichloroethene and tetrachloroethene). The available information on the further transformations of the "first-generation" products of these gas-phase

Table 1. Calculated Tropospheric Lifetimes of Selected Volatile Organic Compounds of Anthropogenic Origin Due to Photolysis and Reaction with OH and NO<sub>3</sub> Radicals and O<sub>3</sub>

Organic	Lifetime due to reaction with <sup>a</sup>			hv <sup>b</sup>
	OH	NO <sub>3</sub>	O <sub>3</sub>	
Ethane	60 days	>12 yr	>4500 yr	
Propane	13 days	>2.5 yr	>4500 yr	
n-Butane	6.1 days	>2.5 yr	>4500 yr	
n-Octane	1.8 days	260 days	>4500 yr	
Ethene	1.8 days	225 days	9.7 days	
Propene	7.0 hr	4.9 days	1.5 days	
Acetylene	19 days	≥2.5 yr	5.8 yr	
Formaldehyde	1.6 days	77 days	>4.5 yr	4 hr
Acetaldehyde	1.0 days	17 days	>4.5 yr	5 days
Acetone	68 days	c	>4.5 yr	15 days
Methyl ethyl ketone	13.4 days	c	>4.5 yr	d
Methanol	17 days	>77 days	c	
Ethanol	4.7 days	>51 days	c	
Methyl t-butyl ether	5.5 days	c	c	
Benzene	12.5 days	>6 yr	>4.5 yr	
Toluene	2.6 days	1.9 yr	>4.5 yr	
m-Xylene	7.8 hr	200 days	>4.5 yr	

<sup>a</sup>OH; average 12-hr concentration of  $1.5 \times 10^6$  molecule cm<sup>-3</sup> (Prinn et al., 1987); NO<sub>3</sub>, average 12-hr concentration of  $5 \times 10^8$  molecule cm<sup>-3</sup> (Atkinson, 1991); O<sub>3</sub>, average 24-hr concentration of  $7 \times 10^{11}$  molecule cm<sup>-3</sup> (Logan, 1985). Calculated from room temperature rate constant and photolysis data of Atkinson (1988, 1990a, 1991) and Rogers (1990).

<sup>b</sup>Unimportant unless noted.

<sup>c</sup>Expected to be of negligible importance.

<sup>d</sup>Expected to be of minor importance.

organic compounds will also be noted. The alkanes, alkenes and aromatic hydrocarbons are the major constituents of vehicle exhaust and also of the gas-phase organic matter observed in polluted air (Grosjean and Fung, 1984; Lonneman et al., 1986; Sigsby et al., 1987; Zweidinger et al., 1988; Stump et al., 1989). The dominance of the alkanes, alkenes and aromatics is demonstrated by Table 2 which shows the speciated ambient air data collected in Los Angeles by Grosjean and Fung (1984). The carbonyl compounds listed in Table 2 are generally formed in the atmosphere [see Atkinson et al. (1990a) for a discussion concerning direct emissions versus atmospheric formation of formaldehyde and acetaldehyde].

Table 2. Hydrocarbons and Carbonyls in Los Angeles Air (from Grosjean and Fung, 1984)

Compound	Range of concentrations ppbv
<u>Alkynes</u>	
acetylene	26-94
<u>Alkanes</u>	
ethane	32-221
propane	11-99
isobutane	10-33
n-butane	21-70
isopentane	23-83
n-pentane	9-34
2,3-dimethylbutane	2-8
2-methylpentane	8-28
3-methylpentane	4-15
n-hexane	5-20
2,2,3-trimethylbutane	0-9
2,4-dimethylpentane	2-6
2,3-dimethylpentane	2-9
3-methylhexane	3-24
2,2,4-trimethylpentane	3-15
n-heptane	3-11
2,5-dimethylhexane	1-3
2,3,4-trimethylpentane	2-5
3-methylheptane	2-5
2,2,5-trimethylhexane	1-4
n-octane	1-5
n-nonane	1-3
n-decane	1-9

Table 2 (continued) - 2

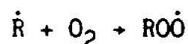
Compound	Range of concentrations ppbv
<u>Cycloalkanes</u>	
methylcyclopentane	4-16
cyclohexane	7-31
dimethylcyclopentane	1-19
methylcyclohexane	3-14
dimethylcyclohexane	0-1
<u>Alkenes</u>	
ethylene	32-91
propene	7-32
1-pentene	1-8
2-methyl-1-pentene	0-4
<u>Aromatics</u>	
benzene	12-29
toluene	20-68
ethylbenzene	3-12
m- and p-xylene	11-45
o-xylene	4-13
n-propylbenzene	1-3
p-ethyltoluene	4-12
o-ethyltoluene	3-1
1,3,5-trimethylbenzene	4-12
1,2,4-trimethylbenzene	4-12
1,2,3-trimethylbenzene	1-4
n-butylbenzene	0-2
<u>Carbonyls</u>	
formaldehyde	4-86
acetaldehyde	2-39
propanal + acetone + acrolein	1-54
n-butanal	0-5
benzaldehyde	0-2

## ALKANE TRANSFORMATION PRODUCTS

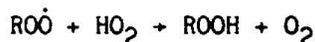
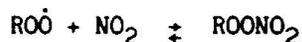
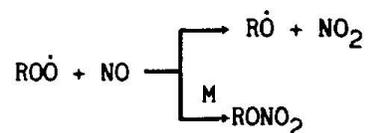
The alkanes react only with the OH radical in the troposphere (Atkinson, 1988, 1990a). The initial reaction proceeds by H atom abstraction to form an alkyl radical



The subsequent reactions have been discussed in detail in the literature (Carter and Atkinson, 1985; Atkinson, 1990a,b) and are generally as follows:

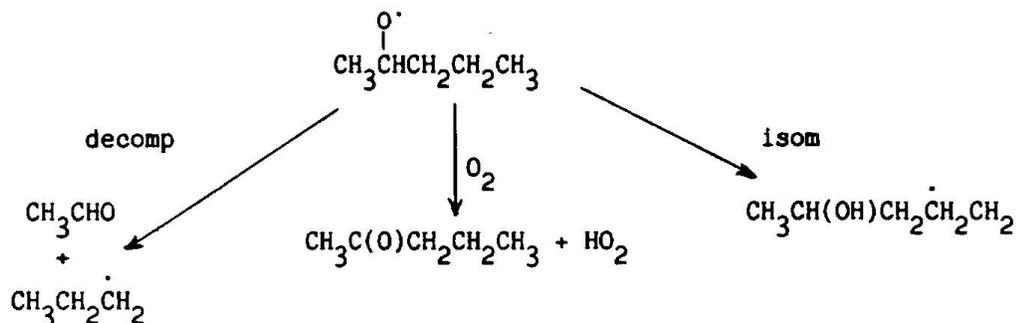


These alkyl peroxy (RO $\dot{\text{O}}$ ) radicals can then react by several pathways:



(where R $_{-1}$ CHO has the same total number of carbon atoms as RO $\dot{\text{O}}$  and  $\alpha + \beta + \gamma = 1$ ).

The above reactions form, at least in part, the alkoxy (R $\dot{\text{O}}$ ) radical. The alkoxy radicals can thermally decompose, react with O $_2$  (if an  $\alpha$ -H is present), or unimolecularly isomerize via a 5-H shift. For example, for the 2-pentoxy radical formed from n-pentane:



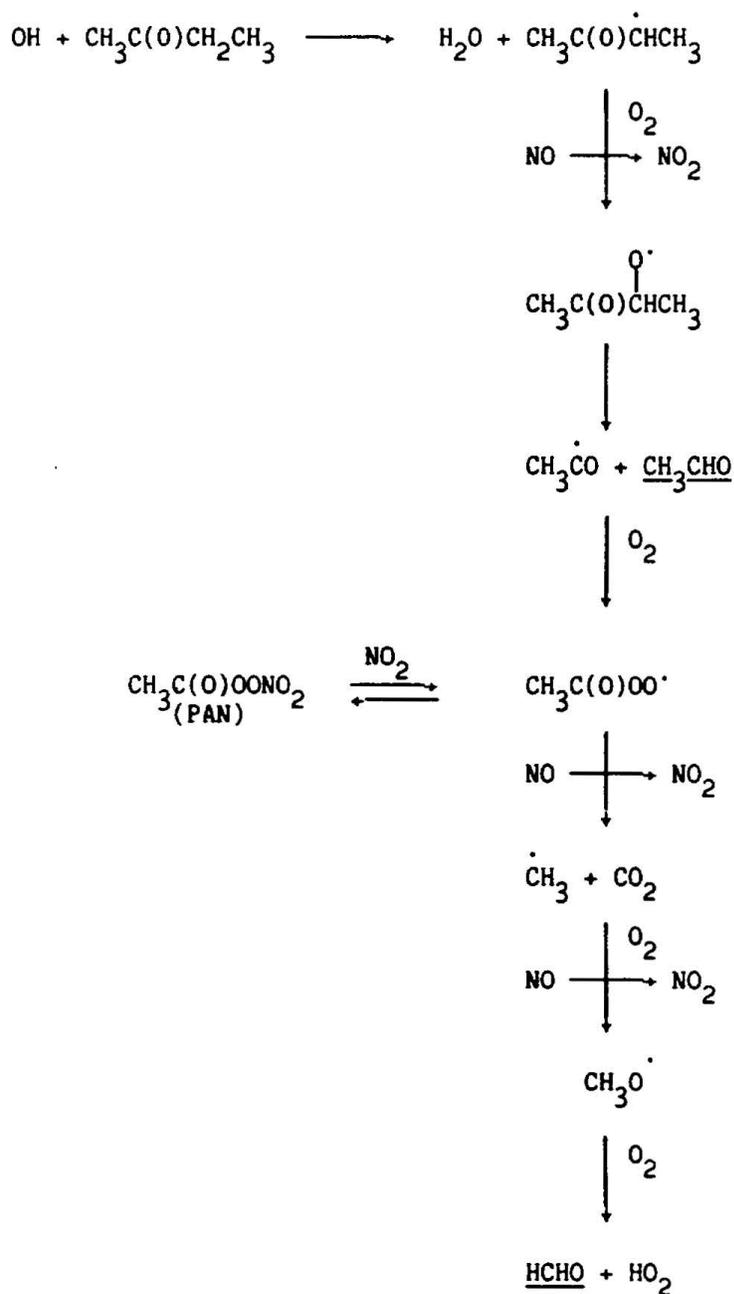
Thus, the decomposition and  $\text{O}_2$  reactions lead to the formation of carbonyl compounds, either aldehydes or ketones. The reactions subsequent to the isomerization reactions have not been elucidated, but are expected to lead to the formation of  $\delta$ -hydroxycarbonyls (for example,  $\text{CH}_3\text{C}(\text{O})\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$  from the 2-pentoxyl radical).

Based on these reaction sequences, the expected "first-generation" products from the atmospheric degradation reactions of the alkanes are shown in Table 3 (with the formation yields being qualitatively ranked as high, medium or low).

Table 3. Expected "First-Generation" Products from the Atmospheric Reactions of Alkanes

Product	Yield	Examples
Carbonyls	high	formaldehyde, acetaldehyde, acetone, methyl ethyl ketone
$\delta$ -Hydroxycarbonyls	medium/high	4-hydroxybutanal
Alkyl nitrates	low/medium	2-butyl nitrate
Hydroperoxides	low in urban areas	methyl hydroperoxide ( $\text{CH}_3\text{OOH}$ )
Alcohols	low	methanol, ethanol

These "first-generation" products react further in the atmosphere, with the majority of them leading to the production of lower molecular weight aldehydes and ketones. For example, the "first-generation" degradation carbonyl products from n-butane are  $\text{CH}_3\text{CHO}$  and  $\text{CH}_3\text{C}(\text{O})\text{CH}_2\text{CH}_3$  from the 2-butoxy radical and  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CHO}$  and  $\text{HOCH}_2\text{CH}_2\text{CH}_2\text{CHO}$  from the 1-butoxy radical. Taking methyl ethyl ketone (2-butanone,  $\text{CH}_3\text{C}(\text{O})\text{CH}_2\text{CH}_3$ ) as an example, its atmospheric reactions and products formed ("stable" products are underlined) are:





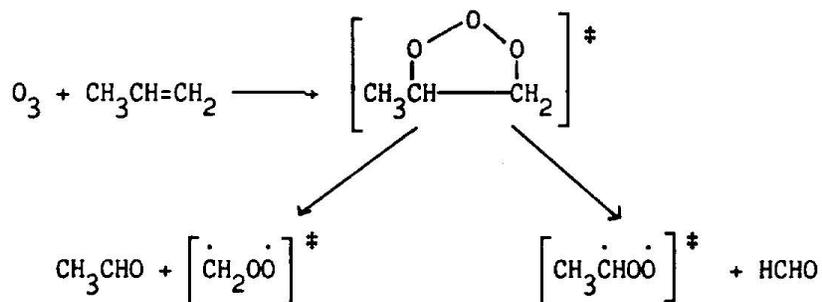
the alkoxy radicals appearing to dominate for the alkenes apart from ethene. For propene, Shepson et al. (1985) observed nitrate formation, analogous to the situation for the OH radical-initiated reactions of the alkanes (see above). Hence the reaction products are:

- Aldehydes such as formaldehyde, acetaldehyde
- Ketones such as acetone
- Hydroxycarbonyls such as glycolaldehyde (HOCH<sub>2</sub>CHO)
- Organic hydroxynitrates such as CH<sub>3</sub>CH(ONO<sub>2</sub>)CH<sub>2</sub>OH and CH<sub>3</sub>CH(OH)CH<sub>2</sub>ONO<sub>2</sub>

Preliminary product data for 1-octene indicates a poor carbon balance (Atkinson, Arey and Aschmann, unpublished data, 1991; Paulson and Seinfeld, 1992), and it is possible that hydroxycarbonyls and/or other polar compounds are formed but are not amenable to the gas chromatographic analysis techniques employed in product identification (see also Tuazon and Atkinson, 1990).

### O<sub>3</sub> Reaction

The initial reaction involves addition of O<sub>3</sub> to the >C=C< bond to form an ozonide, which rapidly decomposes (Atkinson and Lloyd, 1984).



where [ ]<sup>‡</sup> indicates an energy-rich species. The initially energy-rich biradicals such as [CH<sub>3</sub>CHOO]<sup>‡</sup> can decompose or be collisionally stabilized (Atkinson, 1990a; Horie and Moortgat, 1991), and significant uncertainties still exist concerning the formation yields of the energy-rich biradicals and their subsequent reactions. It is also becoming evident that OH

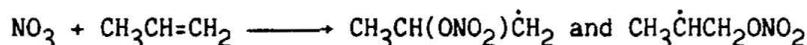
radicals are formed in these O<sub>3</sub> - alkene reactions, with high yields in many cases (Paulson et al., 1992; Atkinson et al., 1992; Horie and Moortgat, 1991). Based on the available product studies and our current knowledge of the reaction mechanisms, the expected products from the gas-phase reactions of O<sub>3</sub> with alkenes are:

- Aldehydes such as formaldehyde and acetaldehyde
- Ketones such as acetone
- Organic acids such as formic acid (HCOOH)
- Hydroperoxides such as methyl hydroperoxide (CH<sub>3</sub>OOH) and hydroxymethyl hydroperoxide (HOCH<sub>2</sub>OOH)
- Other oxygenates including esters and hydroxycarbonyls

In the presence of NO<sub>2</sub>, PAN is a potential product from O<sub>3</sub> - alkene reactions through the intermediacy of the CH<sub>3</sub>ĊO radical.

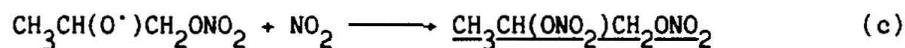
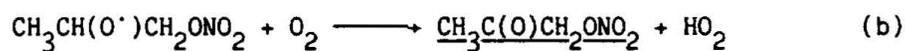
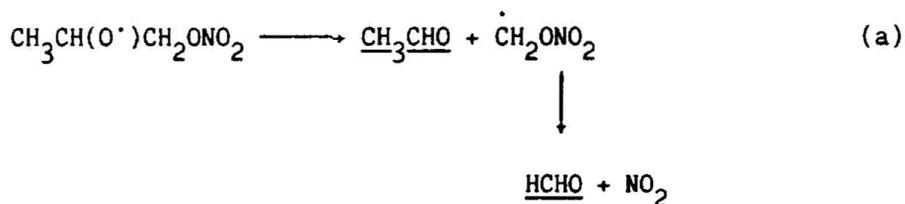
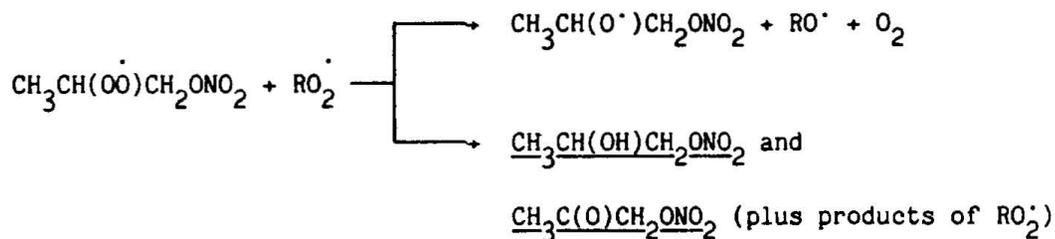
### NO<sub>3</sub> Radical Reactions

As for the OH radical reactions, the NO<sub>3</sub> radical reactions with alkenes proceed by initial addition. The products of the NO<sub>3</sub> radical reactions with several alkenes of anthropogenic origin have been studied at atmospheric pressure (but often at much higher NO<sub>2</sub> concentrations than applicable to the troposphere) by Hoshino et al. (1978), Akimoto et al. (1978), Bandow et al. (1980), Shepson et al. (1985), Barnes et al. (1990) and Hjorth et al. (1990). Based on these data, the likely reaction sequences have been discussed by Atkinson (1991), and under tropospheric conditions the expected reactions for propene are ("stable" products are underlined):



followed by (for the CH<sub>3</sub>ĊHCH<sub>2</sub>ONO<sub>2</sub> radical):



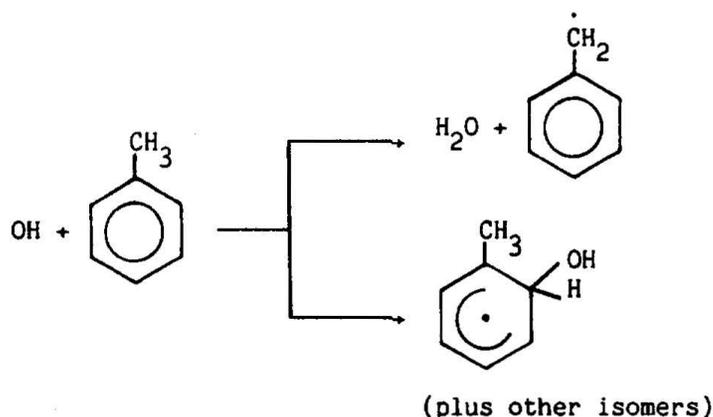


It is expected that under tropospheric conditions, reaction (c) will be of minor or negligible importance. Hence the classes of products formed from the alkenes are:

- Aldehydes such as formaldehyde and acetaldehyde
- Ketones such as acetone
- Carbonyl nitrates such as  $\text{CH}_3\text{C}(\text{O})\text{CH}_2\text{ONO}_2$  and  $\text{CH}_3\text{C}(\text{ONO}_2)\text{CHO}$
- Hydroxynitrates such as  $\text{CH}_3\text{CH}(\text{OH})\text{CH}_2\text{ONO}_2$  and  $\text{CH}_3\text{CH}(\text{ONO}_2)\text{CH}_2\text{OH}$
- Dinitrates such as  $\text{CH}_3\text{CH}(\text{ONO}_2)\text{CH}_2\text{ONO}_2$ .

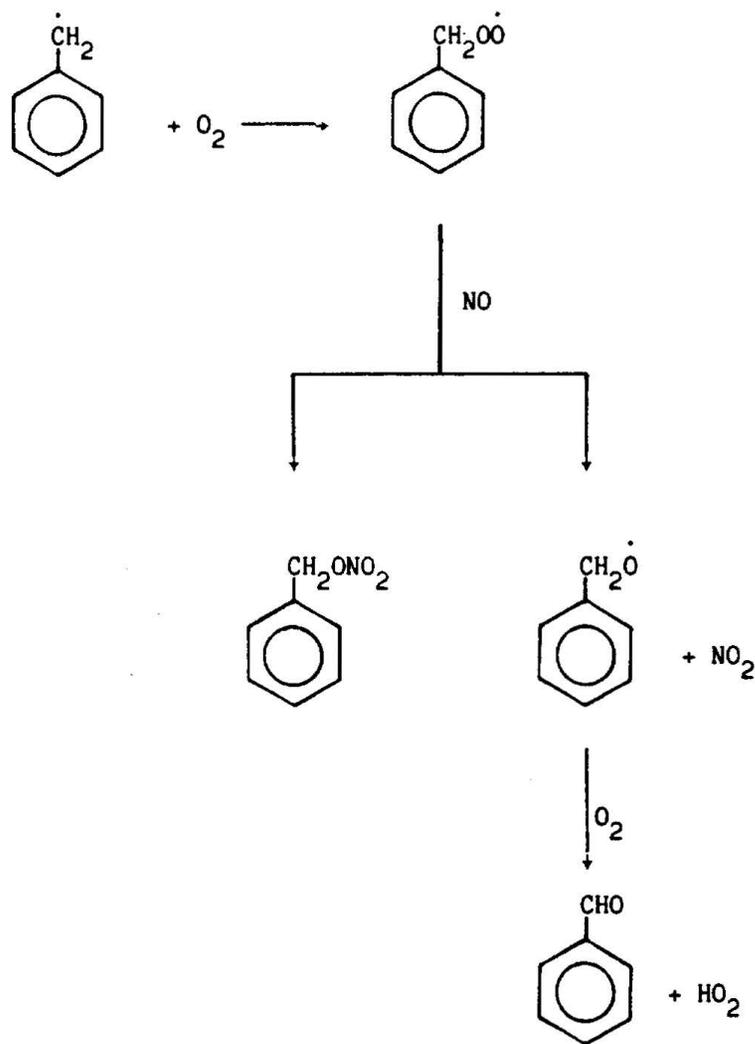
## AROMATIC HYDROCARBON TRANSFORMATION PRODUCTS

Benzene and the alkyl-substituted benzenes such as toluene and the xylenes react in the troposphere essentially only with the OH radical (Table 1). These reactions proceed by two routes; initial OH radical addition to the aromatic ring and H-atom abstraction from the alkyl substituent groups [or, for benzene, from the ring C-H bonds] (Atkinson, 1989, 1990a)



The kinetics and relative importances of these two reaction pathways are well understood (Atkinson, 1989), and the H-atom abstraction channel accounts for  $\leq 10\%$  of the overall reaction rate constant at room temperature and atmospheric pressure (Atkinson, 1989).

The reaction mechanisms and products formed subsequent to the H-atom abstraction channel have also been elucidated (Atkinson, 1990a). Taking the benzyl radical formed from toluene as an example:



Hence the products formed from the aromatic hydrocarbons by this H-atom abstraction channel are:

- Aromatic aldehydes such as benzaldehyde and the tolualdehydes
- Nitrates such as benzyl nitrate and the methyl benzyl nitrates

Unfortunately, the reactions subsequent to the OH radical addition step are not well understood (Atkinson et al., 1989; Knispel et al., 1990;

Atkinson, 1990a), and the relative importance of the reactions of the OH-aromatic adduct (hydroxycyclohexadienyl-type radicals) with  $O_2$  and  $NO_2$  under tropospheric conditions is not quantitatively known at the present time (it appears very possible that the reaction with  $NO_2$  dominates). However, product studies have provided a list of products and in some cases the product yields (Atkinson, 1990a; Atkinson et al., 1991). The classes of products expected are given below

- Phenolic compounds, such as phenol, cresols and dimethylphenols
- Nitrophenols, such as the nitrophenols and nitrocresols  
(formed from subsequent reactions of the phenols and cresols)
- Dihydroxyaromatics such as 1,2-dihydroxybenzene (formed from subsequent reactions of the phenols and cresols)
- $\alpha$ -Dicarbonyls, such as glyoxal, methylglyoxal and 2,3-butanedione
- Nitroaromatics, such as nitrotoluenes, nitrobenzene
- Unsaturated carbonyl and/or hydroxycarbonyls (Dumdei and O'Brien, 1984)

To date, a significant fraction of the products have not been identified and/or quantified, and therefore we do not have a complete mass balance on the products of the atmospheric degradation reactions of aromatic hydrocarbons.

#### POLYCYCLIC AROMATIC HYDROCARBONS

Numerous studies of the atmospheric chemistry of this important class of potential toxic air contaminants have been carried out. The 2- through 4-ring PAH are present at least partially in the gas phase, and can undergo reactions with OH and  $NO_3$  radicals and  $O_3$ . The most important atmospheric loss process is by reaction with the OH radical (Atkinson, 1989; Arey et al., 1989a), similar to the situation for the monocyclic aromatic hydrocarbons. Only a small fraction of the products have been identified and quantified (Arey et al., 1989b; Atkinson et al., 1990b). To date, the observed products are:

- Hydroxy-substituted PAH (Atkinson et al., 1987)
- Nitro-PAH such as nitronaphthalenes and nitrofluoranthenes
- Nitro-PAH lactones (Helmig et al., 1991)

The nitro-PAH and the nitrophenanthrene lactones are important contributors to the direct acting mutagenicity of ambient air particulate matter (Arey et al., 1988, 1992; Atkinson et al., 1988; Helmig et al., 1992), and these classes of atmospherically formed product species may well be considered toxic air contaminants.

### OXYGENATED ORGANIC COMPOUNDS

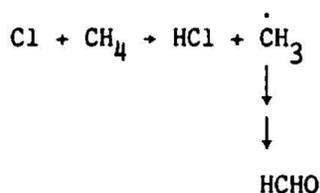
As noted above in the discussions of the products formed from the alkanes, alkenes and aromatic hydrocarbons, a variety of oxygenated organic compounds are produced as "first-generation" products. These compounds may then, of course, react further. Additionally, there are a number of oxygenated species directly emitted into the atmosphere as a result of anthropogenic activities. Formaldehyde and acetaldehyde [both of which are also formed from the atmospheric degradations of other organic compounds (Atkinson et al., 1990a)] may be present in combustion emissions. Methanol, ethanol and various ethers are used as fuel additives to gasolines or reformulated gasolines, and the alcohols may be used as alternative fuels. As discussed by Atkinson (1986, 1990a), the atmospheric degradation of methanol leads to the formation of formaldehyde



and ethanol leads primarily to the formation of acetaldehyde, together with small yields of HCHO and HOCH<sub>2</sub>CHO. Methyl tert-butyl ether reacts with the OH radical in the troposphere to lead mainly to tert-butyl formate [(CH<sub>3</sub>)<sub>3</sub>COCHO] and formaldehyde, together with smaller yields of acetone and methyl acetate (Tuazon et al., 1991). The degradation products of the aldehydes and ketones have been discussed above.

## CHLOROETHENES

The atmospheric chemistry of the chloroethenes has been experimentally investigated by Edney et al. (1986), Tuazon et al. (1988) and Kleindienst et al. (1988). The major tropospheric loss process for the chloroethenes is by reaction with the OH radical. In general, the reaction schemes are similar to those for the alkenes, although to date a complete product distribution has not been achieved. For the more chlorinated compounds such as tri- and tetra-chloroethene, Cl atom formation is important (Edney et al., 1986; Kleindienst et al., 1988; Tuazon et al., 1988). In the atmosphere, this Cl atom formation will lead mainly to the generation of HCl and formaldehyde from the reaction



The products expected to be formed in the troposphere from the chloroethenes include:

- formaldehyde
- formyl chloride (HC(O)Cl)
- phosgene (COCl<sub>2</sub>)
- chlorinated hydroxycarbonyls such as HOCCl<sub>2</sub>C(O)Cl

## CONCLUSIONS

The mechanisms for the atmospheric formation of toxic organic air pollutants have been discussed. Examples of the organic compounds expected or known to be formed for the atmospheric reactions of directly emitted organic compounds have been given. The health effects of these atmospherically formed compounds must be taken into account along with the effects of the parent compounds. For many of these compounds, their formation in the atmosphere dominates over direct emissions. Examples of

toxic organic air pollutants which are being considered by the ARB and which are present in the atmosphere largely due to atmospheric reactions are formaldehyde, acetaldehyde and the nitro-PAH. The organic compounds known or expected to be formed in the atmosphere from anthropogenically emitted organic compounds are listed by class in Table 4.

Table 4. Classes of Organic Compounds Formed in the Atmosphere from Anthropogenic Emissions

Organic Class	Examples
Aldehydes	formaldehyde (HCHO) acetaldehyde (CH <sub>3</sub> CHO)
1,2-Hydroxyaldehydes	glycolaldehyde (HOCH <sub>2</sub> CHO)
1,4-Hydroxyaldehydes	4-hydroxybutanal (HOCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CHO)
Aromatic aldehydes	benzaldehyde (C <sub>6</sub> H <sub>5</sub> CHO)
α,β-Unsaturated aldehydes	acrolein (CH <sub>2</sub> =CHCHO)
Ketones	acetone (CH <sub>3</sub> C(O)CH <sub>3</sub> ) methyl ethyl ketone (CH <sub>3</sub> C(O)CH <sub>2</sub> CH <sub>3</sub> )
1,4-Hydroxyketones	CH <sub>3</sub> C(O)CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> OH
Alkyl nitrates	2-butyl nitrate (CH <sub>3</sub> CH(ONO <sub>2</sub> )CH <sub>2</sub> CH <sub>3</sub> ) 2-pentyl nitrate (CH <sub>3</sub> CH(ONO <sub>2</sub> )CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub> ) 3-pentyl nitrate (CH <sub>3</sub> CH <sub>2</sub> CH(ONO <sub>2</sub> )CH <sub>2</sub> CH <sub>3</sub> )
1,2-Hydroxynitrates	CH <sub>3</sub> CH(OH)CH <sub>2</sub> ONO <sub>2</sub>
1,2-Carbonyl nitrates	CH <sub>3</sub> C(O)CH <sub>2</sub> ONO <sub>2</sub> CH <sub>3</sub> CH(ONO <sub>2</sub> )CHO
Phenolic compounds	phenol (C <sub>6</sub> H <sub>5</sub> OH) o-cresol (ortho-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> OH) 1,2-dihydroxybenzene (C <sub>6</sub> H <sub>4</sub> (OH) <sub>2</sub> ) 2-hydroxybiphenyl
Nitroaromatics	m-nitrotoluene nitrobenzene 3-nitrobiphenyl 2-nitrofluoranthene
Hydroxynitro-aromatics	2-nitrophenol 4-nitrophenol hydroxynitrotoluenes hydroxynitronaphthalenes
Acyl peroxy nitrates	peroxyacetylnitrate (CH <sub>3</sub> C(O)OONO <sub>2</sub> ) peroxypropionyl nitrate (CH <sub>3</sub> CH <sub>2</sub> C(O)OONO <sub>2</sub> ) peroxybenzoyl nitrate (C <sub>6</sub> H <sub>5</sub> C(O)OONO <sub>2</sub> )

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# APPENDIX C

## ATMOSPHERIC FORMATION OF ACROLEIN

Report to the California Air Resources Board  
in partial fulfillment of Contract No. ARB 032-055

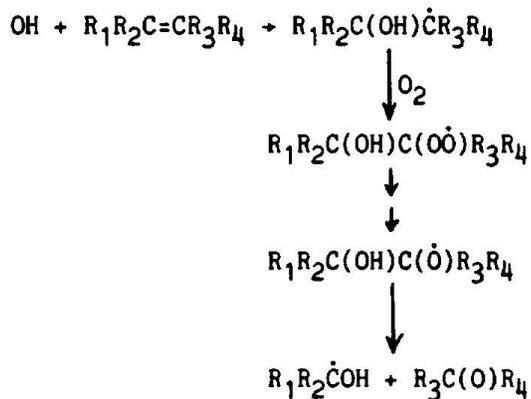
Roger Atkinson and Janet Arey

Statewide Air Pollution Research Center  
University of California  
Riverside, CA 92521

February 1993

## Introduction

Acrolein [CH<sub>2</sub>=CHCHO] is on the California Air Resources Board's list of potential Toxic Air Contaminants. As for several identified or potential Toxic Air Contaminants, in addition to any direct emissions into the atmosphere, acrolein can also be formed in situ in the atmosphere. As currently understood, organic chemicals present in the atmosphere in the gas phase can undergo photolysis and reaction with OH radicals, NO<sub>3</sub> radicals and O<sub>3</sub> (Atkinson, 1988, 1990, 1993). These OH radical, NO<sub>3</sub> radical and O<sub>3</sub> reactions generally lead, at least in part, to the formation of carbonyl compounds as "first-generation" products. With few exceptions, O<sub>3</sub> reacts only with alkenes containing >C=C< bonds (Atkinson and Carter, 1984; Atkinson, 1993). Moreover, alkenes are much more reactive than alkanes towards the NO<sub>3</sub> radical (Atkinson, 1991) and to a lesser extent this is also the case for the OH radical reactions (Atkinson, 1989). The OH radical, NO<sub>3</sub> radical and O<sub>3</sub> reactions with alkenes are often complex, but the major routes to formation of carbonyl compounds involves ultimate cleavage of the >C=C< bond(s). For example, for the OH radical reaction:

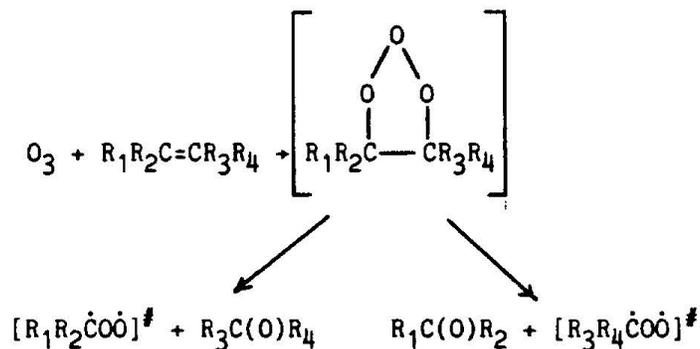


followed by reaction of the  $\alpha$ -hydroxy radical with  $O_2$ ,



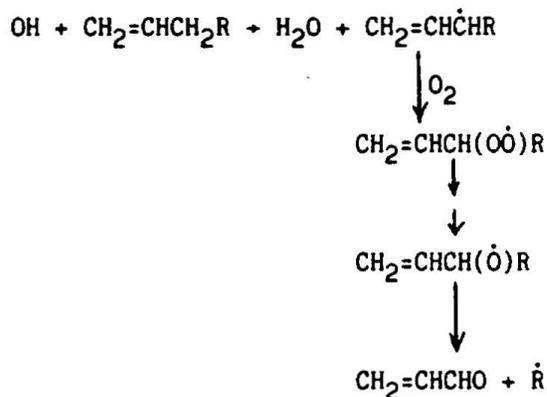
leading to the formation of those carbonyl compounds expected from cleavage of the  $>C=C<$  bond. A generally similar reaction scheme is expected for the  $NO_3$  radical reaction (Atkinson, 1991).

The  $O_3$  reactions with alkenes proceed by initial addition to form an ozonide, which then rapidly decomposes to carbonyls and the corresponding biradicals:



again leading in part to the carbonyl compounds expected from cleavage of the  $>C=C<$  bond.

Hence the formation of acrolein will occur from a precursor organic of the general structure  $CH_2=CHCH=CR_1R_2$ , where  $R_1, R_2 = H$ , alkyl or a substituted alkyl group. In theory, the OH radical reaction could also form acrolein via H-atom abstraction from a compound of structure  $CH_2=CHCH_2-R$ .



However, H-atom abstraction from the C-H bonds of the  $-\text{CH}_2-$  group in  $\text{CH}_2=\text{CHCH}_2\text{R}$  is expected to be an order of magnitude slower than OH radical addition to the  $>\text{C}=\text{C}<$  bond in  $\text{CH}_2=\text{CHCH}=\text{CR}_1\text{R}_2$  (Atkinson, 1989).

It is therefore expected, based on our current understanding of the atmospheric chemistry of organic compounds, that acrolein will be produced in the atmosphere from precursor compounds of structure  $\text{CH}_2=\text{CHCH}=\text{CR}_1\text{R}_2$  ( $\text{R}_1, \text{R}_2 = \text{H}, \text{alkyl}$  or substituted alkyl). The simplest precursor compound is then 1,3-butadiene,  $\text{CH}_2=\text{CHCH}=\text{CH}_2$ , with the 1,3-dienes such as 1,3-pentadiene and 1,3-hexadiene also being precursors to acrolein. Indeed, acrolein has been observed as a product of the  $\text{NO}_x$ -air photooxidation of 1,3-butadiene by Maldotti et al. (1980), in approximately unit yield.

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# APPENDIX D

## ATMOSPHERIC LIFETIME AND FATE OF DI(2-ETHYLHEXYL)PHTHALATE

A Draft Report Submitted in Partial Fulfillment of  
California Air Resources Board Contract No. A032-055

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

Roger Atkinson and Janet Arey

September 1992

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## 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 include:

- Photolysis during daylight hours
- Reaction with the hydroxyl (OH) radical during daylight hours
- Reaction with the hydroperoxyl (HO<sub>2</sub>) radical, mainly during afternoon/evening hours
- Reaction with the nitrate (NO<sub>3</sub>) radical during nighttime hours
- Reaction with nitrogen dioxide (NO<sub>2</sub>)
- Reaction with ozone (O<sub>3</sub>)
- Reaction with gaseous nitric acid (HNO<sub>3</sub>)

For the great majority of organic compounds which are present in the gas phase, the most important of these loss processes remain photolysis and reaction with hydroxyl (OH) and nitrate (NO<sub>3</sub>) radicals and with ozone (O<sub>3</sub>).

However, for a limited number of gaseous 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<sub>2</sub> radicals react with formaldehyde and, more slowly, with acetaldehyde and glyoxal; NO<sub>2</sub> reacts with dialkenes; and gaseous HNO<sub>3</sub> reacts with basic compounds such as the amines.

For chemical compounds present in the adsorbed phase, photolysis and reaction with O<sub>3</sub>, N<sub>2</sub>O<sub>5</sub>, NO<sub>2</sub>, HNO<sub>3</sub>, HONO, H<sub>2</sub>SO<sub>4</sub> and hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) 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 (Bidleman, 1988; Atkinson, 1988).

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

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

where  $\tau_{\text{chemical}}$  and  $\tau_{\text{physical}}$  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

$$\frac{1}{\tau_{\text{chemical}}} = \frac{1}{\tau_{\text{photolysis}}} + \frac{1}{\tau_{\text{OH}}} + \frac{1}{\tau_{\text{NO}_3}} + \frac{1}{\tau_{\text{O}_3}} \dots \quad (2)$$

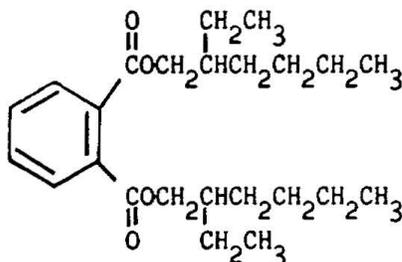
where  $\tau_{\text{photolysis}}$ ,  $\tau_{\text{OH}}$ ,  $\tau_{\text{NO}_3}$  and  $\tau_{\text{O}_3}$  are the lifetimes with respect to photolysis, reaction with the OH radical, reaction with the  $\text{NO}_3$  radical, and reaction with  $\text{O}_3$ , respectively. In turn, these reactive loss processes are determined by the rate constants,  $k_x$ , for reaction and the ambient atmospheric concentrations,  $[X]$ , of the reactive intermediates. For example

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

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

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

In this report, we describe the available literature data concerning the physical and chemical removal processes for di(2-ethylhexyl)phthalate (DEHP):



DEHP is a liquid at room temperature, with a melting point of  $-50^{\circ}\text{C}$  (Aldrich Chemical Company, 1990-91; Mackay, 1991).

#### Gas/Particle Distribution of DEHP in the Atmosphere

Based on the data cited by Mackay (1991), the vapor pressure of DEHP at 298 K is  $2.7 \times 10^{-5}$  Pa or  $2 \times 10^{-7}$  Torr, although Howard et al. (1985) measured a vapor pressure of  $\sim 6.5 \times 10^{-6}$  Torr at 298 K. Bidleman (1988) has shown from theoretical considerations and ambient atmospheric measurements that organic compounds with liquid phase vapor pressures  $>10^{-6}$  Torr at ambient atmospheric temperatures (i.e., at the temperature of the air parcel being considered) exist primarily in the gas phase, and that organic compounds with liquid-phase vapor pressures  $<10^{-8}$  Torr are totally particle-associated in the atmosphere. Using the vapor pressure given by Mackay (1991), these conclusions lead to the expectation that DEHP will exist mainly [-75% based on Figure 3 of Bidleman (1988)] in the particle phase in the atmosphere. The ambient atmospheric measurements of Ligocki et al. (1985a,b) are reasonably consistent with these conclusions of Bidleman (1988). Thus, Ligocki et al. (1985a) did not observe DEHP at detectable levels in the gas phase during several rain events in Portland, OR, but did observe DEHP in the rainwater from gas and particle scavenging by the rainwater as well as DEHP in the air in the particle phase (Ligocki

et al., 1985a,b). The data of Ligocki et al. (1985a,b) allow a value of 65-95% to be obtained for the percentage of DEHP present in the atmosphere in the particle phase under the conditions of their sampling. [Note that the data of Ligocki et al. (1985a,b) lead to the percentages of other phthalates present in the particle phase of: diethylphthalate (and dibutylphthalate), 0%; butylbenzylphthalate, 25%; and dioctylphthalate, 56%].

Atlas and Giam (1981) observed DEHP and di-n-butylphthalate to be present in the atmosphere largely in the gas phase during sampling at Enewetak Atoll in the North Pacific Ocean, with a gas-phase DEHP concentration of (0.3-2.7) ng m<sup>-3</sup>, with similar concentrations being measured in the North Atlantic and the Gulf of Mexico (Atlas and Giam, 1981).

Therefore, it appears that DEHP exists in the atmosphere partitioned between the gas and particle phases, with the possibility being that in urban areas the partitioning is towards the particle phase, with the partitioning being towards the gas phase in remote areas. Such behavior is expected (Pankow and Bidleman, 1991), since the general equation relating gas-particle partitioning is

$$K = A(TSP)/F$$

where K is the gas/particle partition coefficient, A and F are the concentrations in the gas and particle phases, respectively (in the same concentration units), and TSP is the concentration of total suspended particulate matter. Hence as the TSP increases, so must F/A, the particle-associated/gas-phase concentration ratio.

In order to assess the atmospheric behavior of DEHP, the lifetime and fate of DEHP in both the gas and particle phases need to be understood.

The processes to be considered are then:

- Physical loss processes for the particles on which, or in which, DEHP resides.
- Adsorbed-phase reactions of DEHP on the particles.
- Physical loss processes of gas-phase DEHP.
- Photolysis and/or chemical reactions of gas-phase DEHP.

## B. Physical Loss Processes of Particle-Phase DEHP

The particles with which DEHP is associated will undergo wet and dry deposition. The average atmospheric lifetimes for particles due to dry deposition as a function of particle diameter, as presented by Graedel and Weschler (1981), are given in Table 1. The particles with which DEHP are associated are those present in the atmosphere, which based on surface area have a particle size range of ~0.1-5  $\mu\text{m}$  (Finlayson-Pitts and Pitts, 1986). Hence the atmospheric lifetime of these particles due to dry deposition is expected to be of the order of 10-15 days.

In the case of wet deposition, a Washout Ratio  $W_p$ , defined as,

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

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

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

where  $J$  is the precipitation rate. For particles of 0.1-10  $\mu\text{m}$  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  $10^{5\pm 1}$  (Eisenreich et al., 1981; Ligocki et al., 1985b; Bidleman, 1988). Ligocki et al. (1985b) determined a washout ratio for particle-associated DEHP,  $W_p$ , of  $W_p = 2.0 \times 10^4$ , consistent with the washout ratios for particle-associated organic compounds. With a washout ratio of this magnitude, efficient 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 DEHP lifetimes in the winter months than during the summertime.

Thus, considering only its physical atmospheric removal processes, the lifetime of particle-associated DEHP due to particle dry deposition is expected to be around 10-15 days, with an additional efficient, but episodic, removal process involving the rain-out of particles.

Table 1. Average Atmospheric Lifetimes for Particles Due to Dry Deposition (From Graedel and Weschler, 1981)

---

Diameter ( $\mu\text{m}$ )	Lifetime (days)
0.002	0.01
0.02	1
0.2	10
2	10
20	1
200	0.01

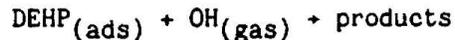
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C. Chemical Loss Processes of Particle-Adsorbed DEHP

In addition to the physical removal of the particles with which the DEHP is associated, the DEHP can also be transformed by a number of chemical processes in the adsorbed phase. These include photolysis and reaction with  $\text{O}_3$ ,  $\text{SO}_2$ ,  $\text{NO}_2$  and/or  $\text{HNO}_3$  and  $\text{N}_2\text{O}_5$ .

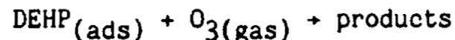
To date, the only data concerning photolysis and chemical reaction of adsorbed DEHP are those of Behnke et al. (1987a). Behnke et al. (1987a) coated various metal oxide aerosols ( $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$  and  $\text{TiO}_2$ ),  $\text{SiO}_2$  aerosol,  $\text{NaCl}$  aerosol and fly ash from a coal power plant with DEHP and investigated the effects of exposing these aerosols to simulated sunlight, OH radicals and  $\text{O}_3$  in a 24000 liter aerosol smog chamber. For DEHP coated on  $\text{NaCl}$  particles and on the fly ash, evidence for volatilization was observed. In the presence of varying OH radical concentrations, generated from the photolysis of  $\text{NO}_x$ -organic-air or  $\text{CH}_3\text{ONO-NO}_x$ -organic-air mixtures, the DEHP decay rates increased approximately linearly with the OH radical concentration for the DEHP-coated  $\text{SO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$  and fly ash particles [no data were obtained for the  $\text{NaCl}$  particles due to the rapid volatilization of DEHP, and a rapid DEHP loss was observed for the  $\text{TiO}_2$  particles (Behnke et al., 1987a) possibly due to the semi-conducting properties of  $\text{TiO}_2$  (Behnke et al., 1988)]. The data obtained lead to an

effective "rate coefficient"  $k$  for the process



of  $k \sim 1 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .

No increase in the DEHP decay rate on  $\text{SiO}_2$  aerosol particles was observed (Behnke et al., 1987a) in the presence of  $2.4 \times 10^{13} \text{ molecule cm}^{-3}$  (1 part-per-million mixing ratio) of  $\text{O}_3$ , leading to an upper limit for the "rate coefficient" for the process



of  $< 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .

It should be noted that the DEHP was coated onto the particles (at concentrations corresponding to less than a monolayer) and was hence available for reaction, and that this study was conducted at low relative humidities (<5%). These aerosols do not mimic the ambient atmospheric particulate matter which is much more chemically complex and may well have several monolayers of water. In this regard, Behnke et al. (1987b) have observed that the heterogeneous degradation of alkanes on  $\text{TiO}_2$  aerosol became less important as the relative humidity increased from <5% to 70%.

#### D. Physical Loss Processes of Gas-Phase DEHP

The expected physical loss process of gas-phase DEHP are wet and dry deposition. No data exist concerning dry deposition of gas-phase DEHP. Ligocki et al. (1985a) did not observe gas-phase DEHP during rain events and hence could not obtain a washout ratio for gas-phase DEHP. However, DEHP which had been in the gas phase was observed in the rain samples collected, indicating efficient rain-out of gas-phase DEHP. They concluded that the dominant wet deposition process for atmospheric DEHP was the rainwater scavenging of particle-associated DEHP (Ligocki et al., 1985b). Bidleman (1988) gives a calculated washout ratio for gas-phase DEHP of  $W_g = 3 \times 10^4$  at 293 K from the Henry's Law constant for DEHP [which may be compared with the value of  $W_g = 9.5 \times 10^4$  at 298 K calculated using the vapor pressure and aqueous solubility given in Mackay (1991)]. A washout ratio of this magnitude is not inconsistent with the

data of Ligocki et al. (1985a), where gas-phase DEHP was observed to be scavenged into rain water during rain events, but was not present in the atmosphere in the gas-phase. In contrast, Atlas and Giam (1981) reported washout ratios for di-n-butylphthalate and DEHP of 34-38 from their rain and air samples collected at Enewetak Atoll in the North Pacific ocean, some 3 orders of magnitude lower than anticipated from the Henry's Law constant.

#### E. Chemical Loss Processes of Gas-Phase DEHP

As noted above, the potential atmospheric chemical loss processes for gas-phase DEHP are photolysis, reaction with the OH radical, reaction with the NO<sub>3</sub> radical and reaction with O<sub>3</sub>. No information is available concerning the gas-phase photolysis of DEHP. Based on the literature data base for O<sub>3</sub> reactions with organic compounds (Atkinson and Carter, 1984; Atkinson, 1993), it is expected that DEHP will not react with O<sub>3</sub> in the gas phase, and that

$$k[\text{O}_3 + \text{DEHP}_{(\text{gas})}] < 10^{-20} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at room temperature.}$$

DEHP is, however, expected to react with OH and NO<sub>3</sub> radicals (Atkinson, 1989, 1991, 1993). The NO<sub>3</sub> radical reaction is expected to proceed by H-atom abstraction from the C-H bonds of the substituent groups. While no experimental data exist concerning the reaction of the NO<sub>3</sub> radical with gas-phase DEHP, the estimation method of Atkinson (1991) allows a room temperature rate constant of

$$k[\text{NO}_3 + \text{DEHP}_{(\text{gas})}] \sim 9 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at 298 K}$$

to be predicted. Similarly, no experimental data exist concerning the reactions of gas-phase DEHP with the OH radical. The estimation method of Atkinson (1987) indicates that the OH radical reaction with DEHP will proceed almost entirely by H-atom abstraction from the C-H bonds of the two substituent groups, and that (Atkinson, 1987)

$$k[\text{OH} + \text{DEHP}_{(\text{gas})}] = 2.2 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at 298 K.}$$

#### F. Tropospheric Lifetime of DEHP

The partitioning of DEHP between the gas and particle phases means that the tropospheric loss processes of DEHP in both phases need to be taken into account in order to assess the tropospheric lifetime of DEHP. For particle-phase DEHP, the upper bound to the lifetime is due to wet and dry deposition of the particles, with a lifetime of ~10-15 days for dry deposition. Since wet deposition of particles is very efficient, the lifetime of particle-associated DEHP will be much shorter during episodic precipitation events. While there is evidence for chemical losses of DEHP on DEHP-coated model particles (Behnke et al., 1987a), it is not evident that such processes occur to any significant extent in the ambient atmosphere. Thus, under non-precipitation conditions the lifetime of particle-associated DEHP should probably be taken to be ~10-15 days.

Using ambient atmospheric OH radical, NO<sub>3</sub> radical and O<sub>3</sub> concentrations of: OH,  $1.6 \times 10^6$  molecule cm<sup>-3</sup> as a 12-hr daylight average (Prinn et al., 1992); NO<sub>3</sub>,  $5 \times 10^8$  molecule cm<sup>-3</sup> as a 12-hr nighttime average (Atkinson, 1991); and O<sub>3</sub>,  $7 \times 10^{11}$  molecule cm<sup>-3</sup> as a 24-hr average (Logan, 1985), then the estimated rate constants given above lead to calculated lifetimes of gas-phase DEHP of ~8 hr, ~50 days, and >4.5 yr due to reaction with OH radicals, NO<sub>3</sub> radicals, and O<sub>3</sub>, respectively. Clearly, the OH radical reaction is expected to dominate as a gas-phase loss process for DEHP.

In conclusion, it is likely that the lifetime of DEHP in the atmosphere is in the range 1-15 days (noting that gas-phase reaction with the OH radical only occurs during daylight hours), and since DEHP is partitioned mainly into the particle phase under urban conditions the lifetime is possibly several days.

#### G. Atmospheric Formation Processes

There are no atmospheric formation pathways for DEHP.

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# APPENDIX E

## ATMOSPHERIC LIFETIME AND FATE OF N-NITROSOMORPHOLINE

A Draft Report Submitted in Partial Fulfillment of  
California Air Resources Board Contract No. A032-055

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

Roger Atkinson and Janet Arey

October 1992

Statewide Air Pollution Research Center  
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## 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 include:

- Photolysis during daylight hours
- Reaction with the hydroxyl (OH) radical during daylight hours
- Reaction with the hydroperoxyl (HO<sub>2</sub>) radical, mainly during afternoon/evening hours
- Reaction with the nitrate (NO<sub>3</sub>) radical during nighttime hours
- Reaction with nitrogen dioxide (NO<sub>2</sub>)
- Reaction with ozone (O<sub>3</sub>)
- Reaction with gaseous nitric acid (HNO<sub>3</sub>)

For the great majority of organic compounds which are present in the gas phase, the most important of these loss processes remain photolysis and reaction with hydroxyl (OH) and nitrate (NO<sub>3</sub>) radicals and with ozone (O<sub>3</sub>).

However, for a limited number of gaseous 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<sub>2</sub> radicals react with formaldehyde and, more slowly, with acetaldehyde and glyoxal; NO<sub>2</sub> reacts with dialkenes; and gaseous HNO<sub>3</sub> reacts with basic compounds such as the amines.

For chemical compounds present in the adsorbed phase, photolysis and reaction with O<sub>3</sub>, N<sub>2</sub>O<sub>5</sub>, NO<sub>2</sub>, HNO<sub>3</sub>, HONO, H<sub>2</sub>SO<sub>4</sub> and hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) 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 (Bidleman, 1988; Atkinson, 1988).

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

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

where  $\tau_{\text{chemical}}$  and  $\tau_{\text{physical}}$  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

$$\frac{1}{\tau_{\text{chemical}}} = \frac{1}{\tau_{\text{photolysis}}} + \frac{1}{\tau_{\text{OH}}} + \frac{1}{\tau_{\text{NO}_3}} + \frac{1}{\tau_{\text{O}_3}} \dots \quad (2)$$

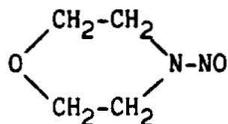
where  $\tau_{\text{photolysis}}$ ,  $\tau_{\text{OH}}$ ,  $\tau_{\text{NO}_3}$  and  $\tau_{\text{O}_3}$  are the lifetimes with respect to photolysis, reaction with the OH radical, reaction with the  $\text{NO}_3$  radical, and reaction with  $\text{O}_3$ , respectively. In turn, these reactive loss processes are determined by the rate constants,  $k_x$ , for reaction and the ambient atmospheric concentrations,  $[X]$ , of the reactive intermediates. For example

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

For photolysis, the photolysis rate depends on the absorption cross section ( $\sigma$ ), the photolysis quantum yield ( $\phi$ ), 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 physical and chemical removal processes for N-nitrosomorpholine



#### Gas/Particle Distribution in the Atmosphere

The vapor pressure of N-nitrosomorpholine has been calculated over the temperature range 273-313 K from thermodynamic theory using the literature vapor pressures at 369 K (6 Torr) and 497-498 K (747 Torr) by Klein (1982). The vapor pressures calculated at 293 K and 313 K were 0.036 Torr and 0.19 Torr, respectively (Klein, 1982), and these lead to an interpolated vapor pressure of N-nitrosomorpholine of 0.055 Torr at 298 K. With a vapor pressure of this magnitude, N-nitrosomorpholine will exist in the atmosphere in the gas phase (Bidleman, 1988), and particle phase reactions of N-nitrosomorpholine can be neglected. For reference, this estimated vapor pressure of N-nitrosomorpholine is similar to that for naphthalene [0.078 Torr at 298 K (Sonnenfeld et al., 1983)], which is present in the gas phase in the atmosphere (Arey et al., 1987, 1989).

#### Atmospheric Loss Processes

No data are available concerning the gas-phase loss processes of N-nitrosomorpholine. The potential loss processes are wet and dry deposition, photolysis and chemical reaction with OH radicals, NO<sub>3</sub> radicals and O<sub>3</sub>. By analogy with N-nitrosodimethylamine (Tuazon et al., 1984), reaction with O<sub>3</sub> is expected to be of no importance, with a rate constant of

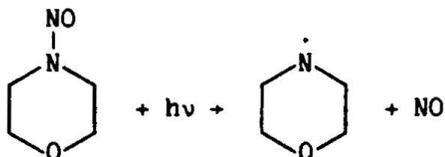
$$k(\text{O}_3 + \text{N-nitrosomorpholine}) < 10^{-20} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K}$$

being expected. Using the estimation method of Atkinson (1987), a rate constant can be calculated for the gas-phase reaction of N-nitrosomorpholine with the OH radical of

$$k(\text{OH} + \text{N-nitrosomorpholine}) \sim 3.5 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

While reaction with the  $\text{NO}_3$  radical is also expected (Atkinson, 1991), no experimental data exist for this reaction and a reliable rate constant cannot be estimated.

By analogy with N,N-dimethylnitrosamine (Tuazon et al., 1984), photolysis may be also important for N-nitrosomorpholine, proceeding by



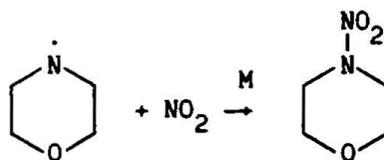
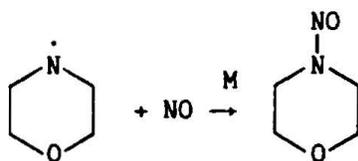
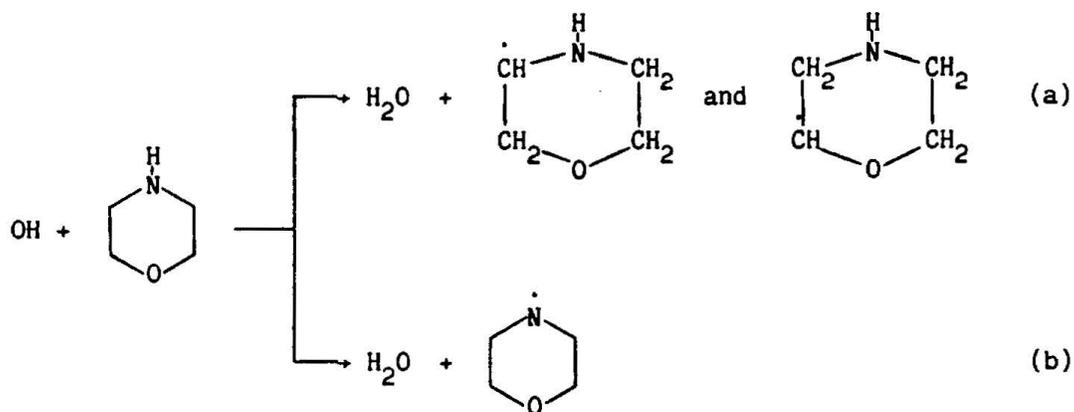
No data are available concerning wet or dry deposition of N-nitrosomorpholine, but these physical processes are anticipated to be of minor importance in comparison with the expected fast chemical atmospheric loss processes (see below).

#### Atmospheric Lifetime of N-Nitrosomorpholine

The calculated lifetime of N-nitrosomorpholine due to OH radical reaction, if the above estimate of the rate constant is correct, is ~5 hr for a 12-hr average OH radical concentration of  $1.6 \times 10^6 \text{ molecule cm}^{-3}$  (Prinn et al., 1992). While it is entirely possible that photolysis will lead to an even shorter lifetime [as is the case for N,N-dimethylnitrosamine (Tuazon et al., 1984)], with the rate constant estimated above the OH radical reaction leads to a short lifetime for N-nitrosomorpholine.

#### Atmospheric Formation of N-Nitrosomorpholine

Based on our current knowledge of atmospheric chemistry, it is expected that N-nitrosomorpholine will be formed in the atmosphere from the OH radical-initiated reaction of morpholine,



with  $k_b \approx 0.25(k_a + k_b)$  based on the estimated overall reaction rate constant of  $(k_a + k_b) \sim 9.5 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (Atkinson, 1987) and the rate constant for the reaction pathway analogous to (b) for dimethylamine (Lindley et al., 1979; Atkinson, 1986). The amino radical is not expected to react with  $\text{O}_2$  (Lindley et al., 1979; Atkinson, 1986), but rather react with  $\text{NO}$  to form N-nitrosomorpholine and with  $\text{NO}_2$  to form the nitramine N-nitromorpholine.

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# APPENDIX F

## ATMOSPHERIC LIFETIME AND FATE OF DIALKYLNITROSAMINES

A Draft Report Submitted in Partial Fulfillment of  
California Air Resources Board Contract No. A032-055

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

Roger Atkinson and Janet Arey

January 1993

Statewide Air Pollution Research Center  
University of California  
Riverside, CA 92521

ARB-93:dialkyl

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## 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 include:

- Photolysis during daylight hours
- Reaction with the hydroxyl (OH) radical during daylight hours
- Reaction with the hydroperoxyl (HO<sub>2</sub>) radical, mainly during afternoon/evening hours
- Reaction with the nitrate (NO<sub>3</sub>) radical during nighttime hours
- Reaction with nitrogen dioxide (NO<sub>2</sub>)
- Reaction with ozone (O<sub>3</sub>)
- Reaction with gaseous nitric acid (HNO<sub>3</sub>)

For the great majority of organic compounds which are present in the gas phase, the most important of these loss processes remain photolysis and reaction with hydroxyl (OH) and nitrate (NO<sub>3</sub>) radicals and with ozone (O<sub>3</sub>).

However, for a limited number of gaseous 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<sub>2</sub> radicals react with formaldehyde and, more slowly, with acetaldehyde and glyoxal; NO<sub>2</sub> reacts with dialkenes; and gaseous HNO<sub>3</sub> reacts with basic compounds such as the amines.

For chemical compounds present in the adsorbed phase, photolysis and reaction with O<sub>3</sub>, N<sub>2</sub>O<sub>5</sub>, NO<sub>2</sub>, HNO<sub>3</sub>, HONO, H<sub>2</sub>SO<sub>4</sub> and hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) 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 (Bidleman, 1988; Atkinson, 1988).

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

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

where  $\tau_{\text{chemical}}$  and  $\tau_{\text{physical}}$  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

$$\frac{1}{\tau_{\text{chemical}}} = \frac{1}{\tau_{\text{photolysis}}} + \frac{1}{\tau_{\text{OH}}} + \frac{1}{\tau_{\text{NO}_3}} + \frac{1}{\tau_{\text{O}_3}} \dots \quad (2)$$

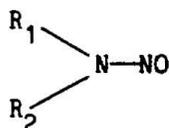
where  $\tau_{\text{photolysis}}$ ,  $\tau_{\text{OH}}$ ,  $\tau_{\text{NO}_3}$  and  $\tau_{\text{O}_3}$  are the lifetimes with respect to photolysis, reaction with the OH radical, reaction with the  $\text{NO}_3$  radical, and reaction with  $\text{O}_3$ , respectively. In turn, these reactive loss processes are determined by the rate constants,  $k_x$ , for reaction and the ambient atmospheric concentrations,  $[X]$ , of the reactive intermediates. For example

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

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

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

In this report, we describe the available literature data concerning the physical and chemical removal processes for dialkylnitrosamines



### Gas/Particle Distribution in the Atmosphere

Klein (1982) has calculated the vapor pressures of a series of dialkylnitrosamines over the temperature range 273-313 K from thermodynamic theory using the literature vapor pressures at elevated temperatures (323-473 K). The vapor pressures calculated at 293 K (Klein, 1982) are given in Table I. These calculated vapor pressures at 293 K are  $\geq 7 \times 10^{-3}$  Torr (Table I). With vapor pressures of this magnitude, these dialkylnitrosamines will exist in the atmosphere in the gas phase (Bidleman, 1988), and particle phase reactions of the dialkylnitrosamines can be neglected. For reference, the vapor pressure of naphthalene, which is present in the gas phase in the atmosphere (Arey et al., 1987, 1989), is 0.078 Torr at 298 K (Sonnenfeld et al., 1983).

### Atmospheric Loss Processes

The only data available concerning the gas-phase loss processes of dialkylnitrosamines are for N-nitrosodimethylamine (Tuazon et al., 1984; Zabarnick et al., 1986). The potential loss processes of the dialkylnitrosamines are wet and dry deposition, photolysis, and chemical reaction with OH radicals, NO<sub>3</sub> radicals and O<sub>3</sub>. By analogy with N-nitrosodimethylamine (Tuazon et al., 1984), for which an upper limit to the rate constant of

$$k(\text{O}_3 + \text{N-nitrosodimethylamine}) \leq 1 \times 10^{-20} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

at  $298 \pm 2$  K has been measured by Tuazon et al. (1984), reactions of the saturated dialkylnitrosamines with O<sub>3</sub> are expected to be of no importance.

Table I. Calculated vapor pressures (Torr) at 293 K for a series of dialkylnitrosamines (from Klein, 1982)

Nitrosamine	Vapor Pressure at 293 K (Torr)
N-Nitrosodimethylamine	2.1
N-Nitrosodiethylamine	0.81
N-Nitrosodi-n-propylamine	0.086
N-Nitrosodi-i-propylamine	0.33
N-Nitrosodi-n-butylamine	0.03
N-Nitrosodi-n-amylamine	0.007
N-Nitrosomethylethylamine	1.1
N-Nitrosomethylbutylamine	0.24
N-Nitrosomethylamylamine	0.1
N-Nitrosoethyl-i-propylamine	0.43
N-Nitrosoethyl-n-butylamine	0.13
N-Nitrosoethyl-t-butylamine	0.37

Rate constants at room temperature have been reported for the reaction of the OH radical with N-nitrosodimethylamine (Tuazon et al., 1984; Zabarnick et al., 1986). Tuazon et al. (1984) used a relative rate method, generating OH radicals from the  $O_3 + N_2H_4$  dark reaction, to obtain a rate constant of

$$k(OH + N\text{-nitrosodimethylamine}) = (2.53 \pm 0.21) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

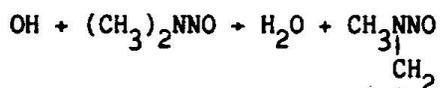
at  $298 \pm 2$  K (Atkinson, 1989). Zabarnick et al. (1986) used a laser photolysis-laser induced fluorescence technique to determine an absolute rate constant for this reaction. The measured rate constant depended on the laser flux, indicating problems from the reactions of the  $(CH_3)_2NNO$  photolysis products. From the data at low laser photolysis fluxes, Zabarnick et al. (1986) reported a rate constant of

$$k(OH + N\text{-nitrosodimethylamine}) = (3.6 \pm 0.1) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

at  $296 \pm 2$  K. The measurements of Tuazon et al. (1984) and Zabarnick et al. (1986) are in reasonable agreement (Atkinson, 1989), and indicate a rate constant of

$$k(OH + N\text{-nitrosodimethylamine}) = 3.0 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

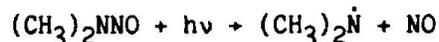
While no product studies of the OH radical-initiated reactions have been carried out to date, these reactions are expected (Atkinson, 1989) to proceed by initial H-atom abstraction from the alkyl group; for example:



While reaction with the  $NO_3$  radical is also expected (Atkinson, 1991), no experimental data exist for these reactions and reliable rate constants cannot be estimated.

By analogy with N-nitrosodimethylamine (Tuazon et al., 1984), photolysis is also expected to be important for the dialkyl nitrosamines. In the actinic region ( $\lambda \geq 290$  nm), N-nitrosodimethylamine has a gas-phase

absorption band in the wavelength region ~310-415 nm, with a maximum absorption cross-section at 363.5 nm (Geiger et al., 1981). For N-nitrosodimethylamine, the photolysis reaction involves breakage of the N-NO bond:

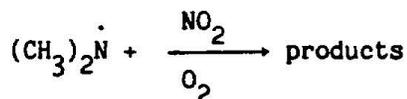
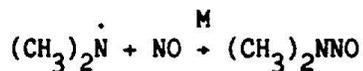
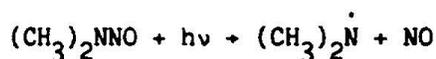


(Tuazon et al., 1984; Geiger et al., 1981), with a photodissociation yield of unity for the wavelength range  $\geq 290$  nm (Geiger et al., 1981; Tuazon et al., 1984). Geiger et al. (1981) measured a photodissociation quantum yield of  $1.03 \pm 0.10$  at 363.5 nm.

No data are available concerning wet or dry deposition of N-nitrosodialkylamines, but these physical processes are anticipated to be of minor importance in comparison with the expected fast chemical atmospheric loss processes (see below).

#### Atmospheric Lifetime of N-Nitrosodimethylamine

The calculated lifetime of N-nitrosodimethylamine due to OH radical reaction is ~5 days for a 12-hr average OH radical concentration of  $1.6 \times 10^6$  molecule  $\text{cm}^{-3}$  (Prinn et al., 1992). In contrast, the photolysis of N-nitrosodimethylamine leads to a calculated lifetime of ~5 min for sunlight at  $0^\circ$  zenith angle (Tuazon et al., 1984) and 8 mins for a  $40^\circ$  zenith solar angle (Lindley et al., 1979). The photolysis reactions are expected to be partially reversible, depending on the NO, NO<sub>2</sub> and O<sub>2</sub> concentrations and the reaction pathways (see also below).



The estimation method proposed by Atkinson (1987) suggests that the OH radical reaction rate constants will be  $\sim 2 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  for N-nitrosodialkylamines with  $(\text{RCH}_2)_2\text{NNO}$  structures and  $\sim 6 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  for N-nitrosodialkylamines with  $(\text{R}_1\text{R}_2\text{CH})_2\text{NNO}$  structures. Such room temperature rate constants lead to lifetimes due to OH radical reaction of  $\sim 9$  hrs and 3 hrs, respectively. Based on these estimates, and assuming that photolysis is as important for the other dialkylnitrosamines, then it appears that the atmospheric lifetimes of the N-nitrosodialkylamines will be dominated by photolysis (Table II), and that during daylight hours the N-nitrosodialkylamines will have a lifetime of only a few minutes.

Table II. Calculated atmospheric lifetimes of N-nitrosodimethylamine due to photolysis and reaction with OH radicals and  $\text{O}_3$

Reaction with	Lifetime
OH <sup>a</sup>	4.8 days
$\text{O}_3$ <sup>b</sup>	>4.5 years
Photolysis <sup>c</sup>	~5 min

<sup>a</sup>For a 12-hr average of  $1.6 \times 10^6 \text{ molecule cm}^{-3}$  (Prinn et al., 1992).

<sup>b</sup>For a 24-hr average of  $7 \times 10^{11} \text{ molecule cm}^{-3}$  (Logan, 1985).

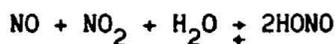
<sup>c</sup>From Tuazon et al. (1984) for  $0^\circ$  zenith angle.

#### Atmospheric Formation of N-Nitrosodialkylamines

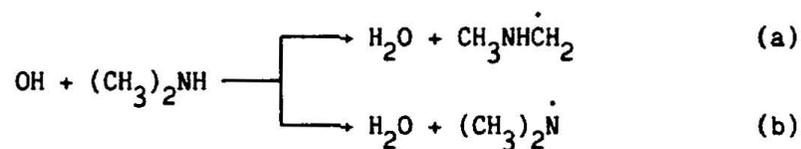
The formation of N-nitrosodialkylamines from the heterogeneous dark reactions of nitrous acid (HONO) with the precursor amine



has been observed (Hanst, 1977; Pitts et al., 1978; Glasson, 1979), with the nitrous acid being formed from the heterogeneous reactions of NO, NO<sub>2</sub> and H<sub>2</sub>O.



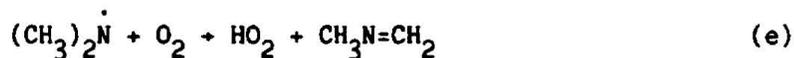
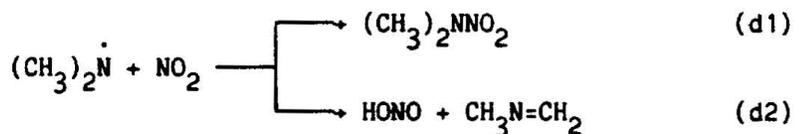
However, it is expected that these heterogeneous surface reactions will be too slow to be a significant source of N-nitrosodialkylamines in the atmosphere (Grosjean, 1991). Thus, based on our current knowledge of atmospheric chemistry, it is expected that N-nitrosodialkylamines will be formed in the atmosphere from the OH radical-initiated reactions of the corresponding dialkylamines. Taking N-nitrosodimethylamine as an example (Lindley et al., 1979; Tuazon et al., 1984)



with process (b) being followed by



in competition with



For the (CH<sub>3</sub>)<sub>2</sub> $\dot{\text{N}}$  radical, Lindley et al. (1979) obtained rate constant ratios of  $k_e/k_c = (1.48 \pm 0.07) \times 10^{-6}$ ;  $k_e/k_{d1} = (3.90 \pm 0.28) \times 10^{-7}$ ; and

$k_{d2}/k_{d1} = 0.22 \pm 0.06$ . These data lead to  $k_c:k_{d1}:k_{d2}:k_e = 1.00:3.8 \pm 0.4:0.84 \pm 0.25:(1.48 \pm 0.07) \times 10^{-7}$ . Additionally, Tuazon et al. (1984) determined that  $k_f/k_{d1} \leq 0.01$ , and hence  $k_f/k_c \leq 0.05$ .

Therefore, it appears that the N-nitrosodialkylamines may be formed slowly during nighttime from the heterogeneous reactions of the precursor amines with NO-NO<sub>2</sub>-H<sub>2</sub>O mixtures (involving HONO) and (expected to be more important) during daylight from the gas-phase OH radical-initiated reactions of the precursor amines in the presence of NO. However, the expected rapid photolysis will limit the levels of the N-nitrosodialkylamines attained in the atmosphere.

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# APPENDIX G

## GAS-PHASE TROPOSPHERIC CHEMISTRY OF ORGANIC COMPOUNDS

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J. Phys. Chem. Ref. Data

In Press (1993)

## Abstract

The gas-phase reactions of selected classes of organic compounds (alkanes, alkenes (including isoprene and monoterpenes), alkynes, aromatic hydrocarbons and oxygen-containing organic compounds and their degradation products) under tropospheric conditions are reviewed and evaluated. The recommendations of the most recent IUPAC evaluation (J. Phys. Chem. Ref. Data 21, 0000, 1992) are used for the  $\leq C_3$  organic compounds, unless more recent data necessitates reevaluation. In addition to the review of the gas-phase tropospheric chemistry of these classes of organic compounds, the previous reviews and evaluations of Atkinson (J. Phys. Chem. Ref. Data, Monograph 1, 1, 1989) for OH radical reactions, Atkinson (J. Phys. Chem. Ref. Data 20, 459, 1991) for  $NO_3$  radical reactions and Atkinson and Carter (Chem. Rev. 84, 437, 1984) for  $O_3$  reactions with organic compounds are updated.

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