

LIFETIMES AND FATES OF TOXIC AIR CONTAMINANTS
IN CALIFORNIA'S ATMOSPHERE

Final Report

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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 |
| GC-MS | Gas chromatography-mass spectrometry |
| i.d. | Internal diameter |
| in | Inch |
| k | Rate constant |
| K | Degrees Kelvin |
| m | Meter |
| M | Third body |
| mm | Millimeter (10^{-3} m) |
| m ³ | Cubic meter |
| MID | Multiple ion detection technique, used together with GC-MS |
| min | Minute |
| m.w. | Molecular weight |
| m/z | Mass to charge ratio |
| NO | Nitric oxide |
| NO ₂ | Nitrogen Dioxide |
| NO _x | Oxides of nitrogen |
| O ₃ | Ozone |
| o.d. | Outer diameter |
| SAPRC | Statewide Air Pollution Research Center |
| s | Second |
| SS | Stainless steel |

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- Epoxyethane
- Styrene
- Diesel exhaust particles and gas- and particle-phase polycyclic aromatic hydrocarbons (PAH) and PAH-derivatives.

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.

B. Experimental Investigation of the Atmospheric Chemistry of Potential Toxic Air Contaminants

As a result of the literature reviews carried out and after consultation with the ARB staff, a limited number of experimental studies were conducted to investigate selected aspects of the atmospheric chemistry of potential toxic air contaminants. The organic compounds, and the aspects of their atmospheric chemistry, studied were: styrene, the kinetics of its reaction with O_3 and the products formed from its reactions with OH and NO_3 radicals and O_3 ; 1,4-dioxane and nitrobenzene, kinetics of their reactions with O_3 ; and p-dichlorobenzene, kinetics of its reactions with NO_3 radicals and O_3 .

The room temperature rate constants k obtained were:

$$k(O_3 + \text{styrene}) = (1.71 \pm 0.18) \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1},$$

$$k(O_3 + 1,4\text{-dioxane}) < 1.5 \times 10^{-20} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1},$$

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

$$k(O_3 + \text{p-dichlorobenzene}) < 5 \times 10^{-21} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

and

$$k(NO_3 + \text{p-dichlorobenzene}) < 4 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

Formaldehyde and benzaldehyde were identified and quantified from the reactions of styrene with OH and NO_3 radicals and O_3 , and plausible reaction sequences formulated.

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 three research tasks were conducted during this program.

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

A literature review of the atmospheric chemistry of each of eight potential toxic air contaminants 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 eight chemicals (or group of chemicals) which were dealt with in this program were (in chronological order):

- Chloroform (trichloromethane).
- 1,3-Butadiene
- Benzo[a]pyrene
- Formaldehyde
- Acetaldehyde

Table I-1. Formation Yields of Aromatic Ring-Retaining Products Formed From the Gas-Phase Reactions of the OH Radical with Benzene, Toluene and the Xylenes Under Simulated Atmospheric Conditions^a

| | Product | Yield |
|----------|------------------------|---|
| Benzene | Phenol | 0.236 ± 0.044 |
| | Nitrobenzene | $\{(0.0336 \pm 0.0078) + (3.07 \pm 0.92) \times 10^{-16} [\text{NO}_2]\}$ |
| Toluene | Benzaldehyde | 0.0645 ± 0.0080 |
| | Benzyl nitrate | 0.0084 ± 0.0017 |
| | o-Cresol | 0.204 ± 0.027 |
| | m- + p-Cresol | 0.048 ± 0.009 |
| | m-Nitrotoluene | $\{(0.0135 \pm 0.0029) + (1.90 \pm 0.25) \times 10^{-16} [\text{NO}_2]\}$ |
| o-Xylene | o-Tolualdehyde | 0.0453 ± 0.0059 |
| | 2-Methylbenzyl nitrate | $\{(0.0135 \pm 0.0051) + (5.5 \pm 4.6) \times 10^{-17} [\text{NO}_2]\}$ |
| | 2,3-Dimethylphenol | 0.097 ± 0.024 |
| | 3,4-Dimethylphenol | 0.064 ± 0.015 |
| | 3-Nitro-o-xylene | 0.0059 ± 0.0018 |
| | 4-Nitro-o-xylene | $\{(0.0111 \pm 0.0029) + (9.9 \pm 2.2) \times 10^{-17} [\text{NO}_2]\}$ |

C. Formation of Hydroxy-, Nitro-, and Hydroxynitro-Aromatics from the Atmospheric Reactions of Aromatic Hydrocarbons

We investigated the aromatic ring-retaining products formed from the OH radical reactions (in the presence of NO_x) with benzene, toluene, and the three xylene isomers, and specifically studied the dependence of the formation yields of these products on the NO and NO_2 concentrations. In addition, we investigated the formation of hydroxynitro-aromatics from the OH and NO_3 radical-initiated reactions of phenol and o-cresol. All reactions were carried out in a 6400-L all-Teflon chamber (ITC), equipped with blacklight irradiation, at 298 ± 2 K and ~740 torr total pressure of dry pure air diluent. The ring-retaining products identified, and their formation yields, from the OH radical-initiated reactions of benzene, toluene and the xylenes are given in Table I-1.

The product data obtained in this study provide important new information concerning the overall mechanisms of the OH radical-initiated reactions of the aromatic hydrocarbons. In particular, these data show that the nitroaromatic formation yields do not extrapolate to zero at low NO_2 concentrations, and it is hence expected that the nitroaromatic (and nitro-polycyclic aromatic hydrocarbons) products of these reactions will be formed under tropospheric conditions, in agreement with the presence in ambient air of a number of nitro-PAH that can only be formed in the atmosphere from the gas-phase reactions of the PAH. We conclude that the initially formed hydroxycyclohexadienyl-type radicals react with NO_2 and not with O_2 , at least for NO_2 concentrations $> 2 \times 10^{13}$ molecule cm^{-3} , and this finding necessitates the development of new chemical mechanisms for the atmospheric chemistry of the aromatic hydrocarbons.

While nitrophenols are formed from both the OH and NO_3 radical-initiated reactions of the phenols and cresols, the formation yields are fairly low, and large concentrations of nitrophenolic compounds are not expected to be formed under atmospheric conditions. For example, the maximum yield of 2-nitrophenol from benzene (under conditions where the initially formed phenol is removed by reaction with the NO_3 radical) is ~3.5-4% of the benzene reacted, and the analogous maximum yield of 2-methyl-6-nitrophenol from toluene is ~1%.

Table I-1 (continued)

| Product | | Yield |
|----------|------------------------|---|
| m-Xylene | m-Tolualdehyde | 0.0331 ± 0.0041 |
| | 3-Methylbenzyl nitrate | 0.0061 ± 0.0027 |
| | 2,4-Dimethylphenol | 0.099 ± 0.023 |
| | 2,6-Dimethylphenol | 0.111 ± 0.033 |
| | 4-Nitro-m-xylene | 0.0018 ± 0.0009 |
| | 5-Nitro-m-xylene | $\{(0.0032 \pm 0.0012) + (1.6 \pm 0.8) \times 10^{-17} [\text{NO}_2]\}$ |
| p-Xylene | p-Tolualdehyde | 0.0701 ± 0.0103 |
| | 4-Methylbenzyl nitrate | 0.0082 ± 0.0016 |
| | 2,5-Dimethylphenol | 0.188 ± 0.038 |
| | 2-Nitro-p-xylene | $\{(0.0120 \pm 0.0035) + (2.8 \pm 2.6) \times 10^{-17} [\text{NO}_2]\}$ |

^aNO₂ concentrations given in molecule cm⁻³ units.

identification phase of a toxic air contaminant involves a parallel effort by the ARB and the DHS, with the DHS 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 DHS 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:

- The available literature data concerning the atmospheric chemistry and ambient concentrations of eight chemical compounds (or group of compounds) which were in the process of review by the ARB as potential toxic air toxics were reviewed, and a report on this subject submitted to the ARB on each chemical (or group of chemicals).
- In cases where necessary information concerning the rates and products of the potentially atmospherically-important reactions was clearly lacking, selected experimental studies were carried out to obtain these data.
- To investigate the atmospheric chemistry of aromatic compounds and the formation of potential toxic air pollutants, the formation of

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 Department of Health Services (DHS). 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

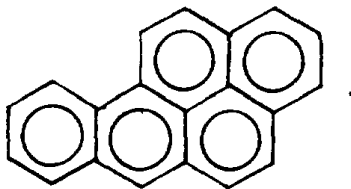
III. LITERATURE REVIEW OF THE ATMOSPHERIC CHEMISTRY OF POTENTIAL TOXIC AIR CONTAMINANTS

A literature review of the atmospheric chemistry of each of eight potential toxic air contaminants 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 eight chemicals (or group of chemicals) which were dealt with in this program were (in chronological order):

(A) Chloroform (trichloromethane), CHCl_3 .

(B) 1,3-Butadiene, $\text{CH}_2=\text{CHCH}=\text{CH}_2$.

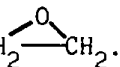
(C) Benzo[a]pyrene,



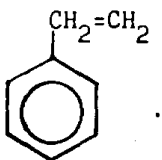
(D) Formaldehyde, HCHO .

(E) Acetaldehyde, CH_3CHO .

(F) Epoxyethane, CH_2-CH_2 .



(G) Styrene,



(H) Diesel exhaust particles and gas- and particle-phase polycyclic aromatic hydrocarbons (PAH) and PAH-derivatives.

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 (NO₃) radical.
- Reaction with ozone (O₃).
- Reaction with the hydroperoxyl (HO₂) radical.

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-phase, 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 (taking the acetaldehyde review as an example):

- Introduction
- Chemical Loss Processes
 - Reaction with Ozone
 - Reaction with the Hydroxyl Radical
 - Reaction with the Nitrate Radical
 - Reaction with the Hydroperoxyl Radical
 - Photolysis

- Physical Loss Processes
- Tropospheric Lifetime and Fate
- Atmospheric Formation
- Ambient Atmospheric Concentrations
- Conclusions
- References

and the reviews as submitted in final form to the ARB (with the references updated, wherever possible, but with no other changes) are given in Appendices A through H.

IV. EXPERIMENTAL INVESTIGATION OF THE ATMOSPHERIC CHEMISTRY OF POTENTIAL TOXIC AIR CONTAMINANTS

As a result of the literature reviews carried out (see Section III above) and after consultation with the ARB staff, a limited number of experimental studies were carried out to investigate selected aspects of the atmospheric chemistry of potential toxic air contaminants. The organic compounds, and the aspects of their atmospheric chemistry, studied were: styrene, the kinetics of its reaction with O_3 and the products formed from its reactions with OH and NO_3 radicals and O_3 ; 1,4-dioxane and nitrobenzene, kinetics of their reactions with O_3 ; and p-dichlorobenzene, kinetics of its reactions with NO_3 radicals and O_3 . These studies are discussed in the sections below.

A. Styrene

The rate constant for the gas-phase reaction of O_3 with styrene was determined at room temperature, and the products of the gas-phase reactions of styrene with OH and NO_3 radicals and O_3 were investigated.

1. Rate Constant for Reaction of Styrene with O_3

The rate constant for the reaction of O_3 with styrene was determined by monitoring the enhanced decay rates of O_3 in the presence of known excess concentrations of styrene. The removal processes of O_3 in this system were (Atkinson et al., 1982a):



Under conditions where $[\text{styrene}] \gg [O_3]_{\text{initial}}$, then

$$-d\ln[O_3]/dt = k_1 + k_2[\text{styrene}] \quad (I)$$

where k_1 is the O_3 decay rate in the absence of added styrene and k_2 is the rate constant for reaction (2). Hence, plots of the O_3 decay rate, $-d\ln[O_3]/dt$, against the styrene concentration should have a slope of k_2 and an intercept of k_1 .

Experiments were carried out in a ~160 liter Teflon reaction chamber which was initially divided into two approximately equal sub-chambers by metal barriers. Ozone was injected into one sub-chamber, and the styrene into the other, each in synthetic air diluent at concentrations designed to achieve the desired initial reactant concentrations in the entire reaction chamber. After the O_3 and the styrene concentrations had been measured in the appropriate sub-chamber, the metal barriers were removed and the contents of the entire reaction chamber mixed for ~1 min. Ozone was monitored throughout the experiments by a Monitor Labs model 8410 chemiluminescence analyzer, while styrene was monitored by gas chromatography with flame ionization detection (GC-FID) using a 10 ft. x 0.125 in. stainless steel column of 10% Carbowax E-600 on C-22 firebrick, operated at 348 K. The initial reactant concentrations were (in units of 10^{13} molecule cm^{-3}): styrene, 0-47; and O_3 , ~1.0-2.4.

The ozone concentrations were monitored for 4-55 min after the contents of the two sub-chambers had been mixed, and in all cases the O_3 decay rates (in the presence of styrene) were exponential over 4-8 half-lives. The results of measurements of styrene concentrations and ozone decay rates are given in chronological order in Table IV-1, and the O_3 decay rates are plotted against the styrene concentration in Figure IV-1. This plot is a good straight line, with the O_3 decay rates in the presence of styrene being two orders of magnitude higher than those in the absence of styrene. A least-squares analysis leads to the rate constant

$$k_2(\text{styrene}) = (1.71 \pm 0.05) \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

at 296 ± 2 K, where the indicated errors are two least-squares standard deviations. Inclusion of an estimated overall uncertainty of $\pm 10\%$ in the GC-FID calibration factor for styrene leads to

$$k_2(\text{styrene}) = (1.71 \pm 0.18) \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

at 296 ± 2 K. This rate constant is in good agreement with our previous room temperature rate constant of $(2.16 \pm 0.46) \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Atkinson et al., 1982a) and in reasonable agreement with the rate constant of $3.0 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 303 K reported by Bufalini and Altshuller (1965).

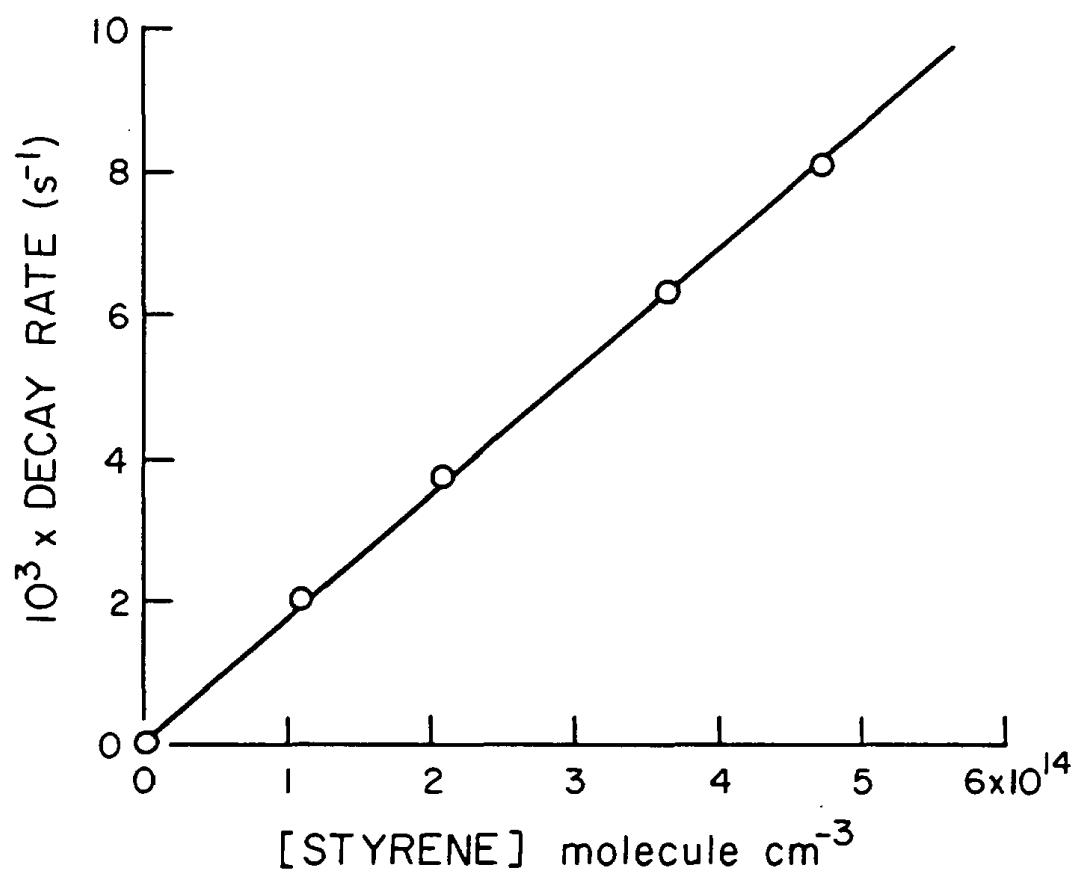


Figure IV-1. Plot of the O_3 decay rate against the styrene concentration.

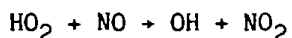
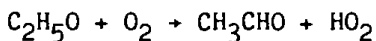
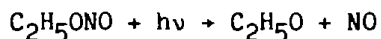
Table IV-1. Ozone Decay Rates in the Presence and Absence of Styrene, 1,4-Dioxane and Nitrobenzene at 296 ± 2 K and ~ 740 Torr Total Pressure of Air

| Organic | Organic Concentration (molecule cm^{-3}) | $10^3 \times \text{O}_3$ Decay Rate (s^{-1}) |
|--------------|---|--|
| | - | 0.0133 |
| Styrene | 2.09×10^{14} | 3.75 |
| | 1.09×10^{14} | 2.07 |
| | 3.63×10^{14} | 6.31 |
| | 4.72×10^{14} | 8.07 |
| | - | 0.0167 |
| 1,4-Dioxane | 1.02×10^{15} | 0.0133 |
| Nitrobenzene | 1.22×10^{15} | 0.0100 |

2. Products of the Reactions of Styrene with OH and NO_3 Radicals and O_3

These experiments to investigate the products formed from the reactions of styrene with OH and NO_3 radicals and O_3 were carried out in a 5800 liter evacuable, Teflon-coated, chamber equipped with a multiple reflection optical system interfaced to a Nicolet 7199 Fourier transform infrared (FT-IR) absorption spectrometer. When desired, radiation was provided by a 24 kW xenon arc. A schematic of this chamber facility is shown in Figure IV-2.

All experiments were carried out at 298 ± 2 K and at atmospheric pressure of air. Hydroxyl radicals were generated by the photolysis of ethyl nitrite in air, with NO being added to suppress the formation of O_3 and of NO_3 radicals



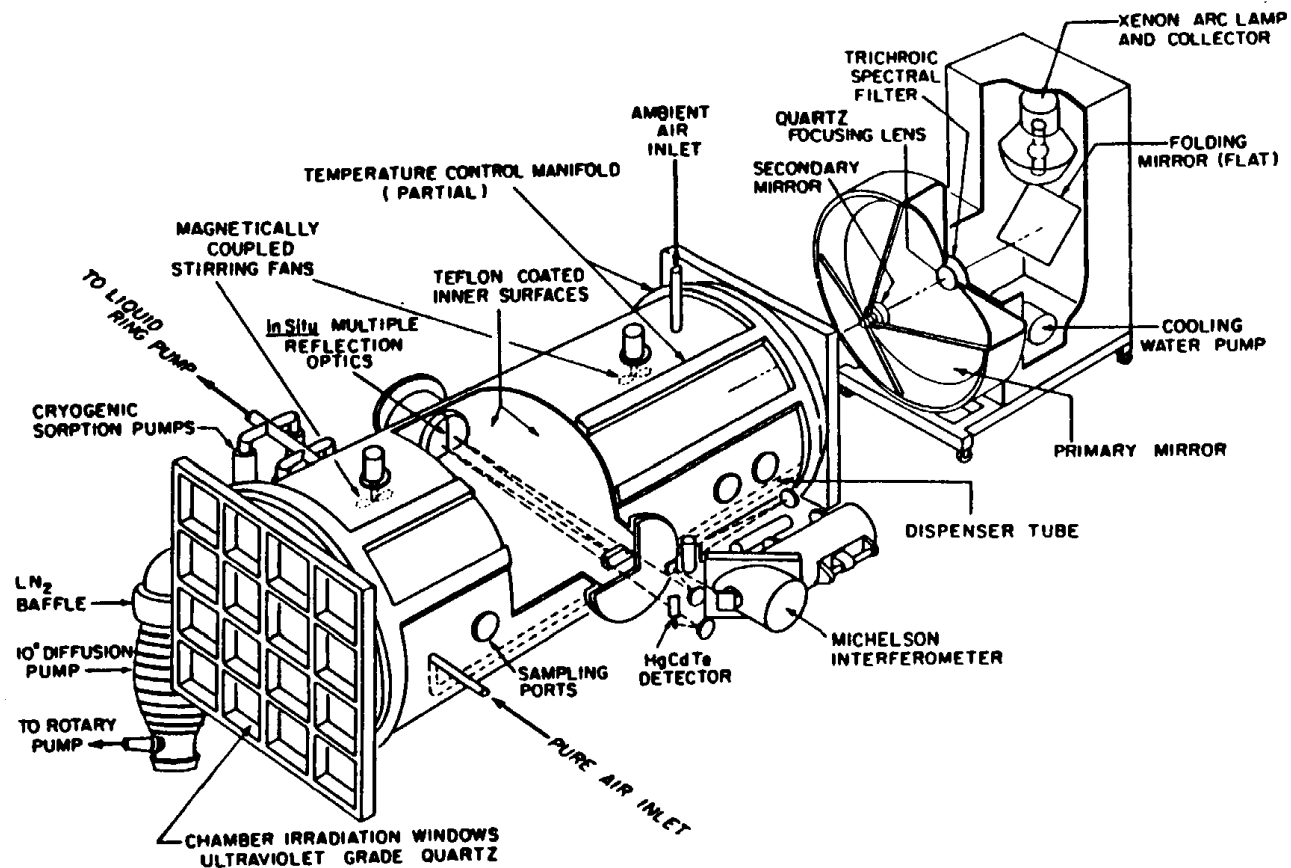
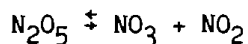


Figure IV-2. Schematic of the 5800 liter SAPRC evacuable chamber facility.

NO₃ radicals were generated from the thermal decomposition of N₂O₅



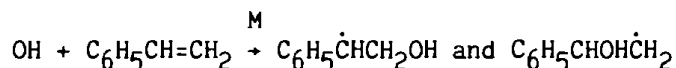
and NO₂ was added to maintain the above equilibrium towards N₂O₅ and to suppress secondary reactions of any radical species formed from the NO₃ radical reaction with styrene. The products and reactants were monitored during the experiments by FT-IR absorption spectroscopy.

Styrene + OH. Duplicate runs (EC-1336 and EC-1337) were carried out which consisted of irradiation of mixtures of styrene (2.4×10^{14} molecule cm⁻³), ethyl nitrite (2.4×10^{14} molecule cm⁻³), and NO (1.9×10^{14} molecule cm⁻³) in air.

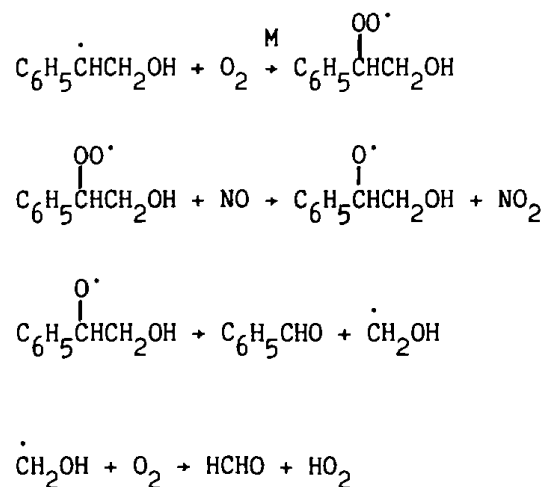
The initial yields of the expected products HCHO and C₆H₅CHO were 90% and ~75%, respectively. These yields declined with irradiation time, owing to the reaction of these products with OH radicals and ensuing secondary reactions. Thus, the decrease in yield of C₆H₅CHO was accounted for in part by the formation and increase in the concentration of peroxybenzoyl nitrate (PBzN) with irradiation time. Another stable product was observed which had a nitrate (-ONO₂) group, as indicated by infrared absorption bands at 1667, 1280, and 848 cm⁻¹. Using the range of values of absorption coefficients normally associated with the -ONO₂ groups of organic compounds, it was estimated that this organic nitrate could possibly equal the amount of styrene consumed which was not accounted for by the amounts of C₆H₅CHO and PBzN formed.

The benzaldehyde formation yield of ~0.75 observed in this work is in reasonable agreement with the formation yield of 1.03 ± 0.15 obtained by Bignozzi et al. (1981) from the time-concentration profiles of styrene and benzaldehyde in an irradiated NO_x - styrene - air mixture.

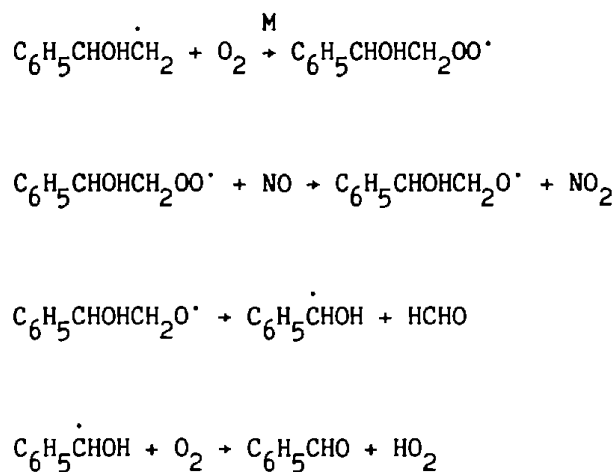
The magnitude of the OH radical reaction rate constant (Atkinson, 1989) suggests that the reaction of the OH radical with styrene proceeds by initial OH radical addition to the substituent -CH=CH₂ group



In the presence of NO, and neglecting the formation of organic nitrates from the reaction of the peroxy radicals with NO, the reactions subsequent to this initial OH radical addition to the -CH=CH₂ group are expected to be (Atkinson, 1990)



and



The observed high, and equal, yields of HCHO and C₆H₅CHO are in general agreement with this reaction scheme.

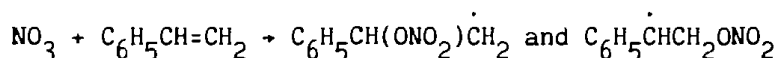
Styrene + NO₃. The dark reaction of N₂O₅ (9.6 × 10¹³ molecule cm⁻³) with styrene (2.4 × 10¹⁴ molecule cm⁻³) in air (EC-1334) resulted in the disappearance of ≥94% of the N₂O₅ after 7 minutes. A similar run which employed 1.2 × 10¹⁴ molecule cm⁻³ of N₂O₅ and 2.4 × 10¹⁴ molecule cm⁻³ of styrene (EC-1335), and which generated a higher amount of NO₂ (i.e., 1.2 ×

10^{14} molecule cm^{-3} vs. 8.9×10^{13} molecule cm^{-3}), resulted in a slower rate of N_2O_5 disappearance ($\geq 98\%$ after 17 min). In both runs, HCHO and $\text{C}_6\text{H}_5\text{CHO}$ were formed in equal yields but in amounts which were only 10-12% of the styrene consumed.

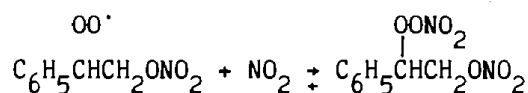
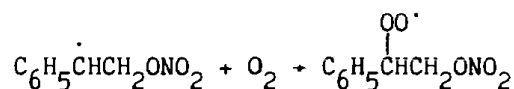
Three unidentified N-containing compounds were the most conspicuous products of the styrene + N_2O_5 system. One of these unknown products (product A) was formed during the very early stage of the reaction but disappeared rapidly. The infrared absorption bands associated with product A indicated that it contained both $-\text{ONO}_2$ (1670, 1281, 846 cm^{-1}) and $-\text{OONO}_2$ (1726, 1297, 790 cm^{-1}) groups. A second unknown (product B) was more stable than product A, but a steady decrease of its concentration with time was also observed. The infrared spectra indicated that product B contained $-\text{ONO}_2$ (1636, 1283, 852 cm^{-1}) and $-\text{C}=\text{O}$ (1701 cm^{-1}) groups. The most stable of the three N-containing unknowns was product C, which had absorption bands attributed to $-\text{ONO}_2$ (1680, 1285, 843 cm^{-1}) and $-\text{C}=\text{O}$ (1729 cm^{-1}) groups.

Formaldehyde, benzaldehyde, product B and product C were the products of styrene present at the time when N_2O_5 was totally consumed. Of the balance of nitrogen not accounted for by NO_2 and HNO_3 formation, 80% in run EC-1334 and 86% in run EC-1335 could be found in products B and C, if it is assumed that the combined amounts of these products were equal to the styrene consumed minus benzaldehyde formed.

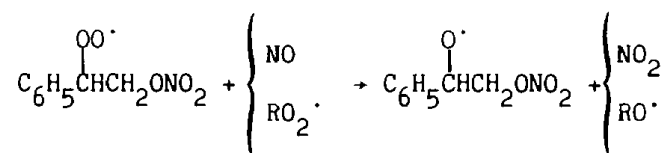
The NO_3 radical reaction with styrene is expected to proceed by initial NO_3 radical addition to the $-\text{CH}=\text{CH}_2$ substituent group:



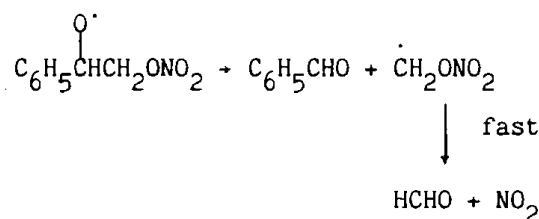
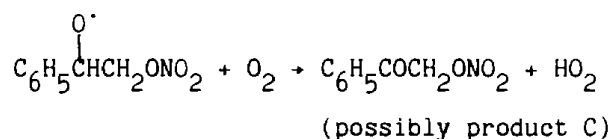
followed by the reactions (taking the $\text{C}_6\text{H}_5\dot{\text{C}}\text{HCH}_2\text{ONO}_2$ radical as an example)



(possibly product A)



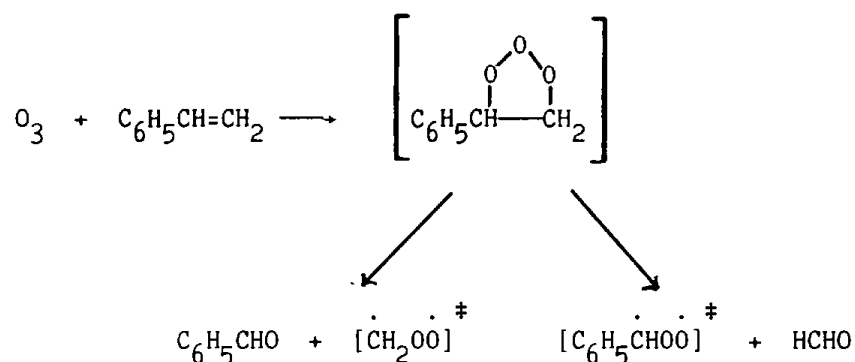
(where the $\text{RO}_2\cdot$ radical can include the $\text{C}_6\text{H}_5\overset{\text{OO}\cdot}{\underset{|}{\text{CH}}}\text{CH}_2\text{ONO}_2$ or $\text{C}_6\text{H}_5\text{CH}(\text{ONO}_2)\text{CH}_2\text{OO}\cdot$ radicals)



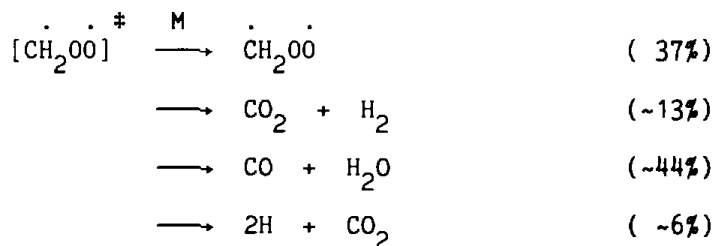
Analogous intermediate or first-generation products [$\text{C}_6\text{H}_5\text{CH}(\text{ONO}_2)\text{CH}_2\text{OONO}_2$ and $\text{C}_6\text{H}_5\text{CH}(\text{ONO}_2)\text{CHO}$] are expected to be formed from the $\text{C}_6\text{H}_5\text{CH}(\text{ONO}_2)\dot{\text{C}}\text{H}_2$ radical.

Styrene + O_3 . Two experiments were carried out for the dark reaction of styrene with ozone: run EC-1332 where 1.2×10^{14} molecule cm^{-3} of O_3 was mixed with 2.4×10^{14} molecule cm^{-3} of styrene in air; and run EC-1333 where 1.2×10^{14} molecule cm^{-3} of styrene was injected into a mixture of 2.4×10^{14} molecule cm^{-3} of O_3 in air. In both cases, $\geq 95\%$ of the reactant with the lesser concentration was consumed after 15 minutes. The reaction proceeded with a 1:1 stoichiometric disappearance of the reactants for both runs. The readily identifiable, major products were HCHO and $\text{C}_6\text{H}_5\text{CHO}$, each with a yield of $\sim 40\%$. HCOOH was a minor product, with a yield of $\sim 1\text{-}2\%$. Unknown products were observed which exhibit overlapped features in the -C=O stretch region ($\sim 1750 \text{ cm}^{-1}$) and other relatively strong, broad bands in the $950\text{-}1450 \text{ cm}^{-1}$ region.

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



where [][‡] denotes an initially energy-rich biradical species. The subsequent reactions of the $[\dot{\text{C}}\text{H}_2\ddot{\text{O}}\dot{\text{O}}]^\ddagger$ radical formed from the O_3 + ethene reaction have been discussed in detail previously (Atkinson and Lloyd, 1984; Atkinson and Carter, 1984; Atkinson, 1990). At atmospheric pressure of air and room temperature



with the thermalized $\dot{\text{C}}\text{H}_2\ddot{\text{O}}\dot{\text{O}}$ biradical being expected to react with water vapor to form HCOOH under atmospheric conditions. The reactions of the $[\text{C}_6\text{H}_5\dot{\text{C}}\text{H}\ddot{\text{O}}\dot{\text{O}}]^\ddagger$ radical are not presently known. The product data obtained are reasonably consistent with the above reaction scheme, providing that the $[\text{C}_6\text{H}_5\dot{\text{C}}\text{H}\ddot{\text{O}}\dot{\text{O}}]^\ddagger$ biradical does not produce $\text{C}_6\text{H}_5\text{CHO}$ in high yield.

3. Rate Constants for the Reactions of 1,4-Dioxane and Nitrobenzene with O_3

Rate constants, or upper limits thereof, were determined for the gas-phase reactions of 1,4-dioxane and nitrobenzene with O_3 at 296 ± 2 K and atmospheric pressure of air. The 1,4-dioxane and nitrobenzene concentrations and the measured O_3 decay rates are given in Table IV-1. The O_3 decay rates in the presence and absence of 1,4-dioxane or nitrobenzene were indistinguishable, and hence only upper limits to the rate constants could be obtained. Assuming that the entire O_3 decay rates observed in

the presence of 1,4-dioxane or nitrobenzene were due to reaction leads to upper limits to the rate constants of

$$k_2(1,4\text{-dioxane}) < 1.5 \times 10^{-20} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

and

$$k_2(\text{nitrobenzene}) < 1 \times 10^{-20} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}.$$

4. Rate Constants for the Reactions of p-Dichlorobenzene with NO₃ Radicals and O₃

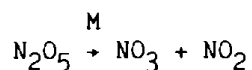
Experiments were carried out in a 5800 liter evacuable chamber (Figure IV-2), with the reactants being monitored during the experiments by long pathlength FT-IR absorption spectroscopy. The experiments were carried out in the dark.

For the O₃ reactions, the decays of p-dichlorobenzene were monitored in the presence of excess concentrations of O₃. Since these conditions are conducive to the occurrence of secondary reactions (Atkinson and Carter, 1984), cyclohexane was added to the reactant mixtures in amounts sufficient to scavenge any OH radicals formed. p-Dichlorobenzene decayed slowly to the chamber walls in the dark in the absence of added O₃, at a rate of $\sim 3.5 \times 10^{-6} \text{ s}^{-1}$, and the observed p-dichlorobenzene decay rates in the presence of $5.1 \times 10^{14} \text{ molecule cm}^{-3}$ of O₃ were actually slightly less than in the absence of O₃. Thus, no evidence of any reaction of p-dichlorobenzene with O₃ was obtained. From the observed p-dichlorobenzene decay rates in the presence of O₃ (uncorrected for wall decay), a very conservative upper limit to the rate constant for the gas-phase reaction of O₃ with p-dichlorobenzene of

$$k_2(\text{O}_3 + \text{p-dichlorobenzene}) < 5 \times 10^{-21} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

at $298 \pm 2 \text{ K}$ was obtained.

An upper limit to the rate constant for the gas-phase reaction of the NO₃ radical with p-dichlorobenzene was obtained using a relative rate technique in which the decay rates of p-dichlorobenzene and a reference organic (cyclohexane in this case) were monitored in the presence of NO₃ radicals. NO₃ radicals were generated from the thermal decomposition of N₂O₅



The decay rates of p-dichlorobenzene after addition of N_2O_5 to the chamber were slower than the p-dichlorobenzene decay rates prior to N_2O_5 addition (which were $3.7 \times 10^{-6} \text{ s}^{-1}$, very similar to the decay rates observed in the O_3 experiments). The amounts of cyclohexane reacted were 5.5-6.2% over the 2.4 hr duration of the reactions, while 1.5% of the p-dichlorobenzene had disappeared from the gas phase. Since this disappearance of p-dichlorobenzene could be totally accounted for by wall decay, no evidence for any gas-phase reaction of p-dichlorobenzene with the NO_3 radical was obtained. From the observed p-dichlorobenzene disappearance from the gas phase and the amounts of cyclohexane reacted, a very conservative upper limit to the rate constant ratio of

$$k(\text{NO}_3 + \text{p-dichlorobenzene})/k(\text{NO}_3 + \text{cyclohexane}) < 0.25$$

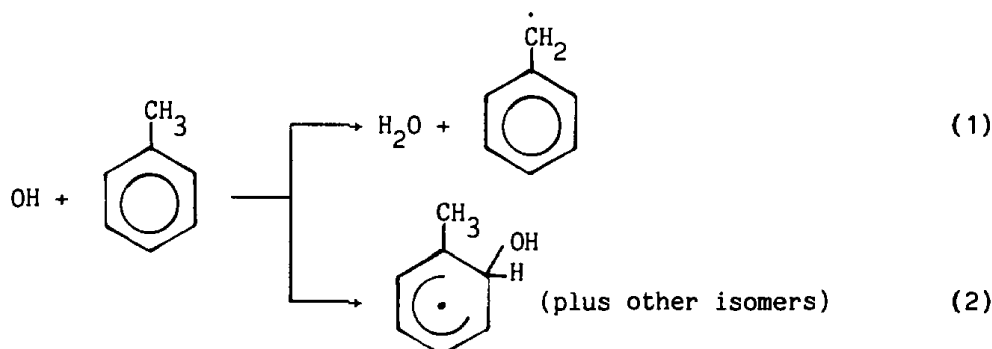
was obtained at $298 \pm 2 \text{ K}$. With a room temperature rate constant for the reaction of the NO_3 radical with cyclohexane of $1.3 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Atkinson et al., 1988), this leads to

$$k(\text{NO}_3 + \text{p-dichlorobenzene}) < 4 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

at $298 \pm 2 \text{ K}$.

V. FORMATION OF HYDROXY-, NITRO- AND HYDROXYNITRO-AROMATICS FROM THE ATMOSPHERIC REACTIONS OF AROMATIC HYDROCARBONS

Aromatic hydrocarbons are important constituents of gasoline fuels (Lonneman et al., 1986; Sigsby et al., 1987) and vehicle emissions (Lonneman et al., 1986; Sigsby et al., 1987; Zweidinger et al., 1988), and comprise a significant fraction of the organic compounds observed in urban atmospheres (Nelson and Quigley, 1984; Grosjean and Fung, 1984). Under tropospheric conditions, the alkyl-substituted benzenes react only with the OH radical (Atkinson, 1988), and the room temperature rate constants for most of these OH radical reactions are reliably known (Atkinson, 1989). At atmospheric pressure and temperatures ≤ 325 K, these OH radical reactions proceed by H-atom abstraction from the alkyl substituent group(s) and the C-H bonds of the aromatic ring [reaction (1)], and by OH radical addition to the aromatic ring [reaction (2)]. For example, for toluene



However, despite numerous studies (see, for example, Hoshino et al., 1978; Darnall et al., 1979; Takagi et al., 1980, 1982; Atkinson et al., 1980, 1983; Shepson et al., 1984; Dumdei and O'Brien, 1984; Tuazon et al., 1984, 1986; Leone et al., 1985; Bandow et al., 1985; Bandow and Washida, 1985a,b; Gery et al., 1985, 1987), the reaction mechanisms subsequent to these initial steps and the products formed under atmospheric conditions, and their yields, are still not well known.

The reactions subsequent to the H-atom abstraction pathway [reaction (1)] under atmospheric conditions lead to the formation of aromatic carbonyls and nitrates (Atkinson and Lloyd, 1984). However, the reactions subsequent to formation of the OH-aromatic adducts [reaction (2)] are much

less well understood. Ring cleavage appears to be the dominant reaction pathway, as evidenced by the formation of α -dicarbonyls and a variety of other oxygenated ring-opened compounds (Darnall et al., 1980; Takagi et al., 1980, 1982; Atkinson et al., 1983; Shepson et al., 1984; Dumdei and O'Brien, 1984; Tuazon et al., 1984, 1986; Bandow et al., 1985; Bandow and Washida 1985a,b; Gery et al., 1985, 1987).

In this work, we investigated the aromatic ring-retaining products formed from the OH radical reactions (in the presence of NO_x) with benzene, toluene, and the three xylene isomers, and specifically studied the dependence of the formation yields of these products on the NO and NO_2 concentrations. In addition, we investigated the formation of hydroxy-nitro-aromatics from the OH and NO_3 radical-initiated reactions of phenol and o-cresol.

A. Product Formation from the OH Radical-Initiated Reactions of Benzene, Toluene and the Xylenes

1. Experimental

All reactions were carried out in a 6400-L all-Teflon chamber (ITC), equipped with blacklight irradiation, at 298 ± 2 K and ~ 740 torr total pressure of dry pure air diluent. Hydroxyl radicals were generated by the photolysis of methyl nitrite in air at wavelengths ≥ 300 nm. NO and NO_2 were also added to the reactant mixtures, which had initial concentrations of (in units of 10^{13} molecule cm^{-3}): CH_3ONO , 2.3-32; NO, 2.1-37; NO_2 , 0-33; aromatic hydrocarbon, 2.4-5.4. The light intensity was maintained at 100% of the maximum intensity, corresponding to an NO_2 photolysis rate of $\sim 8 \times 10^{-3} \text{ s}^{-1}$, and the irradiation times were varied from 0.5-15 min.

The aromatic hydrocarbons were monitored during the experiments by gas chromatography with flame ionization detection (GC-FID), using a 10 ft x 0.125 in. stainless steel column of 10% Carbowax 600 on C-22 firebrick (100/110 mesh), operated at 348 K. After calibration with authentic samples, the aromatic products were quantified by GC-FID, with 100 cm^3 gas samples being collected from the chamber onto Tenax GC solid adsorbent, with subsequent thermal desorption at 525 K onto a 15 m DB-5 Megabore fused silica column held at 333 K, and then temperature programmed from 333 to 523 K at 8 K min^{-1} . Gas samples were also collected onto Tenax GC

mass spectrometry (GC-MS), using a 50 m HP-5 column in a Hewlett-Packard 5890 GC over interfaced to a Hewlett-Packard 5970 Mass Selective Detector operated in the scanning mode.

During these experiments, the NO and the sum of the initial NO and NO₂ concentrations were monitored by a chemiluminescence analyzer, which had a maximum measurement level of 2.4×10^{14} molecule cm⁻³ for either NO or NO_x. Since CH₃ONO was also monitored as (NO_x-NO) by this instrument, only NO could be monitored after the introduction of CH₃ONO into the chamber. In order to obtain reliable estimates for the NO₂ concentrations during the irradiations, computer calculations were carried out using the initial experimental conditions and an up-to-date chemical mechanism incorporating CH₃ONO chemistry, the full array of inorganic reactions and toluene chemistry (Carter, 1990). (Since the chemistry of irradiated CH₃ONO-NO-NO₂-organic-air mixtures is dominated by the CH₃ONO-NO-NO₂-air reactions, the results of these calculations were not significantly dependent on the validity of the aromatic chemistry.)

The sources of the chemicals used, and their stated purities, were as follows: benzene, phenol and benzyl chloride (all Analytical Reagent Grade), Mallinckrodt; toluene (99+%), Matheson, Coleman and Bell; benzaldehyde (98+%), o-cresol (99+%), m-cresol (99+%), p-cresol (99+%), o-nitrotoluene (99+%), m-nitrotoluene (99%), p-nitrotoluene (99%), α-chloro-o-xylene (99%), α-chloro-m-xylene (98%), α-chloro-p-xylene (98%), 2,3-dimethylphenol (97%), 2,4-dimethylphenol (97%), 2,5-dimethylphenol (99+%), 2,6-dimethylphenol (99.8+%), 3,4-dimethylphenol (99%), 3,5-dimethylphenol (99+%), 3-nitro-o-xylene (97%), 4-nitro-o-xylene (99%), 2-nitro-m-xylene (99%), 4-nitro-m-xylene (98%), 5-nitro-m-xylene (99+%), m-tolualdehyde (97%) and p-tolualdehyde (97%), Aldrich Chemical Company; nitrobenzene (reagent ACS grade), Eastman Kodak Company; 2-nitro-p-xylene, Lancaster Synthesis; o-tolualdehyde, Pfaltz and Bauer, Inc.; silver nitrate (99.88%), Anachemia Chemicals Ltd.; NO (99%), Matheson Gas Company. Methyl nitrite was prepared as described by Taylor et al. (1980) and was stored under vacuum at 77 K. NO₂ was prepared by reacting NO with an excess of O₂ prior to introduction into the chamber. Benzyl nitrate and the methylbenzyl nitrates were prepared, in solution, for GC-MS confirmatory purposes from the addition of the corresponding benzyl chloride or α-

chloroxylylene to silver nitrate dissolved in acetonitrile, as described by Ferris et al. (1953).

2. Results

A series of $\text{CH}_3\text{ONO-NO-NO}_2$ -aromatic hydrocarbon-air irradiations were carried out, and the initial reactant concentrations are given in Tables V-1 (benzene), V-2 (toluene), V-3 (o-xylene), V-4 (m-xylene) and V-5 (p-xylene). From retention time matching with authentic samples, the GC analyses showed that phenol and nitrobenzene were formed as products in the $\text{CH}_3\text{ONO-NO-NO}_2$ -benzene-air irradiations. The identity of these two products was confirmed by GC-MS analysis. At longer irradiation times, especially under conditions where the initially present NO was largely consumed (for example, run ITC-1295), other product peaks were observed in the GC analyses, and these were most likely nitrophenols formed from further reaction of the phenol with OH and/or NO_3 radicals.

In an analogous manner, GC analyses of the irradiated $\text{CH}_3\text{ONO-NO-NO}_2$ -toluene-air mixtures showed benzaldehyde, o-cresol, m- + p-cresol (which were not separated on either the 15 m DB-5 Megabore column or the 50-m HP-5 capillary column), m-nitrotoluene and p-nitrotoluene to be products, and these were confirmed by GC-MS. The GC-MS analyses showed that a product peak tentatively identified by GC from retention time matching as o-nitrotoluene was actually a mixture of o-nitrotoluene and benzyl nitrate, with benzyl nitrate being the major constituent of this product peak (these two products were partially resolved on the 50 m HP-5 column). As for the benzene system, at longer irradiation times, especially under conditions where the initially present NO was largely consumed, other product peaks were observed and these were identified as nitrocresols by GC-MS. These nitrocresols were probably formed from OH radical and/or NO_3 radical reactions with the initially formed cresols.

From retention time matching with authentic samples, the GC analyses showed that the products of the $\text{CH}_3\text{ONO-NO-NO}_2$ -xylene-air irradiations were in each case the tolualdehyde, dimethylphenols, nitro-xylenes and the methylbenzyl nitrate, and the identities of these products were confirmed by GC-MS analyses.

The observed concentrations of NO, benzene, phenol and nitrobenzene during the $\text{CH}_3\text{ONO-NO-NO}_2$ -benzene-air irradiations are given in Table V-1, and the observed concentrations of NO, toluene, benzaldehyde, o-cresol, m-

Table V-1. Reactant and Product Concentrations (molecule cm^{-3}) During Irradiated $\text{CH}_3\text{ONO-NO-NO}_2$ -Benzene Air Mixtures

| ITC Run # | 10^{-13} x Concentration | | | | 10^{-11} x Concentration | |
|--------------|----------------------------|------------------|--------------------|---------|----------------------------|-------------------|
| | CH_3ONO^a | NO | NO_2 | Benzene | Phenol | Nitro- benzene |
| 1289 | 24.2 | 24 ^a | 0 ^a | 5.090 | - | - |
| | | 20.5 | [3.5] ^b | 4.805 | 4.27 (7.47) ^c | 2.27 |
| | | 19.2 | [4.8] | 4.622 | 4.47 (10.7) | 2.92 |
| | | 19.7 | [4.3] | 4.514 | 5.66 (16.1) | 2.70 |
| 1290 | 30.1 | 24 ^a | 0 ^a | 5.090 | - | - |
| | | 19.7 | [4.3] | 4.752 | 3.42 (6.56) | 1.90 |
| | | 18.2 | [5.8] | 4.582 | 4.40 (11.3) | 3.02 |
| | | 18.7 | [5.3] | 4.457 | 4.51 (14.0) | 3.26 |
| 1291 | 14.1 | 13.6 | 1.6 | 5.198 | - | - |
| | | 7.7 | [7.5] | 4.858 | 4.68 (8.98) | 1.97 |
| | | 6.4 | [8.8] | 4.666 | 5.28 (13.8) | 2.92 |
| | | 6.3 | [8.9] | 4.562 | 5.36 (16.3) | 2.92 |
| 1292 | 23.7 | 13.7 | 12 ^a | 5.419 | - | - |
| | | 14.4 | [11.3] | 5.162 | 4.34 (6.98) | 2.90 |
| | | 14.5 | [11.2] | 5.018 | 5.15 (10.6) | 3.51 |
| | | 15.6 | [10.1] | 4.922 | 5.08 (12.2) | 3.87 |
| 1293 | 5.2 | 6.5 | 0.67 | 4.733 | - | - |
| | | 3.5 | [3.7] | 4.452 | 4.96 (8.93) | 1.46 |
| | | 2.5 | [4.7] | 4.318 | 5.62 (13.1) | 1.80 |
| | | 2.3 | [4.9] | 4.258 | 5.64 (14.5) | 2.09 |
| 1294 | 26.3 | 24 ^a | 24 ^a | 4.860 | - | - |
| | | ~25 ^d | [23] | 4.762 | 3.08 (3.80) | 1.78 |
| | | ~25 ^d | [23] | 4.656 | 3.74 (5.73) | 2.24 |
| | | ~25 ^d | [23] | 4.596 | 4.04 (6.94) | 2.90 |
| 1295 | 3.0 | 2.6 | 0.46 | 4.862 | - | - |
| | | 0.38 | [2.7] | 4.486 | 6.22 (13.1) | 1.17 |
| | | 0 | [3.1] | 4.356 | 5.55 e | 1.49 |
| | | 0 | [3.1] | 4.277 | 3.08 e | 1.44 |
| 1296 | 5.1 | 2.6 | 2.9 | 4.862 | - | - |
| | | 0.94 | [4.6] | 4.572 | 4.83 (8.77) | 1.83 |
| | | 0.20 | [5.3] | 4.457 | 5.83 e | 2.22 |
| | | 0.10 | [5.4] | 4.370 | 5.47 e | 2.24 |

Table V-1 (continued) - 2

| ITC Run # | 10^{-13} x Concentration | | | | 10^{-11} x Concentration | |
|--------------|----------------------------------|-----------------|-----------------|---------|----------------------------|-------------------|
| | CH ₃ ONO ^a | NO | NO ₂ | Benzene | Phenol | Nitro- benzene |
| 1297 | 12.2 | 6.0 | 7.4 | 4.680 | - | - |
| | | 4.2 | [9.2] | 4.399 | 3.70 (6.72) | 1.68 |
| | | 3.6 | [9.8] | 4.291 | 5.00 (11.1) | 2.75 |
| | | 3.7 | [9.9] | 4.238 | 4.64 (11.3) | 2.12 |
| 1298 | 26.1 | 24 ^a | 0 ^a | 4.980 | - | - |
| | | 20.4 | [3.6] | 4.829 | 3.61 (4.92) | 1.58 |
| | | 19.0 | [5.0] | 4.606 | 4.57 (9.50) | 2.14 |
| | | 20.2 | [3.8] | 4.510 | 4.57 (11.2) | 2.27 |

^aBased upon the amounts introduced to the chamber.

^bValues in [] are the NO₂ concentrations estimated from the NO data, assuming that ([NO] + [NO₂]) = constant (see text).

^cValues in () are corrected for reaction with the OH radical (see text).

^dEstimates from computer modeling of irradiated CH₃ONO-NO-organic-air systems.

^eNO₃ radical reactions also contributing to removal of phenol; corrections cannot be made.

Table V-2. Reactant and Product Concentrations (molecule cm^{-3}) During Irradiated $\text{CH}_3\text{ONO-NO-NO}_2$ -Toluene-Air Mixtures

| ITC Run # | 10^{-13} x Concentration | | | | 10^{-11} x Concentration | | | | | |
|--------------|----------------------------|-----------------|--------------------|---------|----------------------------|--------------|--------------|----------------------------------|-----------------|-----------------|
| | CH_3ONO^a | NO | NO_2 | Toluene | Benzaldehyde | o-Cresol | m + p-Cresol | Benzyl Nitrate + o-Nitro-toluene | m-Nitro-toluene | p-Nitro-toluene |
| 1260 | 24.0 | 24 ^a | ~0 ^a | 4.683 | - | - | - | - | - | - |
| | | 19 ^b | 5 ^b | 4.234 | 3.44 (3.84) ^c | 7.37 (10.2) | 1.23 (1.81) | 0.83 | 2.76 | 0.53 |
| | | 15 ^b | 9 ^b | 3.597 | 6.07 (8.07) | 10.68 (23.7) | 1.59 (4.01) | 1.34 | 4.17 | 1.15 |
| | | 14 ^b | 10 ^b | 3.239 | 6.71 (9.96) | 12.24 (35.4) | 2.10 (7.12) | 1.15 | 3.88 | 1.02 |
| 1261 | 25.4 | 24 ^a | ~0 ^a | 4.514 | - | - | - | - | - | - |
| | | 19 ^b | 5 ^b | 4.098 | 2.91 (3.23) | 6.42 (8.77) | 1.13 (1.64) | 0.45 | 2.22 | 0.51 |
| | | 15 ^b | 9 ^b | 3.519 | 5.46 (7.14) | 11.37 (24.2) | 1.93 (4.64) | 1.10 | 3.21 | 0.86 |
| | | 14 ^b | 10 ^b | 3.186 | 6.57 (9.55) | 12.14 (33.4) | 2.10 (6.75) | 1.50 | 4.28 | 1.18 |
| 1263 | 31.9 | 23.5 | 0.38 | 4.633 | - | - | - | - | 0.13 | - |
| | | 19.3 | [4.3] ^d | 4.132 | 3.30 (3.73) | 6.16 (8.88) | 0.98 (1.51) | 0.83 | 2.03 | 0.40 |
| | | 14.8 | [9.4] | 3.440 | 6.07 (8.36) | 9.73 (23.5) | 1.82 (5.06) | 1.20 | 2.84 | 0.72 |
| | | 13.6 | [11.2] | 3.059 | 6.63 (10.4) | 9.73 (31.6) | 1.62 (6.22) | 2.38 | 4.07 | 1.31 |
| 1264 | 24.7 | 11.0 | 0.89 | 4.427 | - | - | - | - | - | - |
| | | 7.9 | [3.4] | 3.964 | 3.22 (3.63) | 5.80 (8.25) | 1.10 (1.67) | 0.70 | 0.70 | 0.21 |
| | | 4.4 | [7.1] | 3.366 | 5.99 (8.05) | 8.96 (20.4) | 1.64 (4.27) | 1.20 | 2.38 | 0.80 |
| | | 2.7 | [9.1] | 2.999 | 8.15 (12.4) | 9.09 (27.7) | 1.80 (6.44) | 2.03 | 3.10 | 1.20 |
| 1265 | 27.4 | 11.9 | 12.1 | 4.533 | - | - | - | - | - | - |
| | | 11.3 | [13.0] | 4.151 | 2.75 (3.02) | 5.62 (7.47) | 1.00 (1.40) | 0.67 | 1.85 | 0.43 |
| | | 10.4 | [14.7] | 3.538 | 5.33 (6.96) | 9.58 (20.3) | 1.85 (4.43) | 0.99 | 3.02 | 0.78 |
| | | 10.3 | [15.5] | 3.209 | 6.07 (8.80) | e | 2.82 (8.99) | 2.11 | 4.52 | 1.55 |
| 1266 | 24.0 | 6.0 | 5.9 | 4.579 | - | - | - | - | - | - |
| | | 4.8 | [7.2] | 4.151 | 3.00 (3.36) | 5.01 (6.89) | 1.00 (1.46) | 0.40 | 0.94 | 0.24 |
| | | 3.0 | [9.1] | 3.597 | 5.30 (6.87) | 8.70 (18.1) | 1.87 (4.39) | 0.88 | 2.01 | 0.70 |
| | | 1.8 | [10.6] | 3.245 | 6.38 (9.23) | 9.86 (26.9) | 2.05 (6.51) | 1.26 | 2.86 | 0.94 |

Table V-2 (continued) - 2

| ITC Run # | 10 ⁻¹³ x Concentration | | | | 10 ⁻¹¹ x Concentration | | | | | |
|--------------|-----------------------------------|-------|-----------------|---------|-----------------------------------|-------------|--------------|----------------------------------|-----------------|-----------------|
| | CH ₃ ONO ^a | NO | NO ₂ | Toluene | Benzaldehyde | o-Cresol | m + p-Cresol | Benzyl Nitrate + o-Nitro-toluene | m-Nitro-toluene | p-Nitro-toluene |
| 1267 | 10.3 | 5.6 | 6.1 | 4.543 | - | - | - | - | - | - |
| | | 4.4 | [7.2] | 4.176 | 2.69 (2.95) | 4.83 (6.35) | 0.98 (1.36) | 0.43 | 1.04 | 0.35 |
| | | 3.1 | [8.4] | 3.642 | 4.88 (6.19) | 7.88 (15.5) | 1.82 (4.01) | 0.99 | 2.97 | 1.10 |
| | | 2.6 | [9.4] | 3.366 | 5.77 (7.96) | 8.86 (21.6) | 1.90 (5.33) | 1.66 | 3.50 | 1.28 |
| 1268 | 5.0 | 4.4 | 0.24 | 4.662 | - | - | - | - | - | - |
| | | 2.4 | [2.0] | 4.151 | 3.47 (3.93) | 5.34 (7.75) | 1.10 (1.71) | 0.53 | 0.45 | 0.29 |
| | | 0.53 | [3.9] | 3.583 | 6.05 (8.04) | 8.03 (17.8) | 2.05 (5.17) | 1.04 | 2.22 | 1.20 |
| | | 0.02 | [4.1] | 3.292 | 7.02 (10.2) | 8.11 f | 2.57 f | 0.94 | 1.93 | 0.88 |
| 1269 | 5.0 | 2.4 | 2.2 | 4.410 | - | - | - | - | - | - |
| | | 1.3 | [3.1] | 4.039 | 2.69 (2.96) | 4.39 (5.83) | 1.16 (1.63) | 0.35 | 0.67 | 0.27 |
| | | 0.19 | [4.3] | 3.546 | 4.96 (6.27) | 6.73 f | 1.85 f | 0.80 | 1.87 | 0.96 |
| | | 0.02 | [4.3] | 3.313 | 5.91 (8.04) | 6.62 f | 1.82 f | 1.07 | 2.70 | 1.36 |
| 1270 | 2.4 | 2.4 | 0.07 | 4.546 | - | - | - | - | - | - |
| | | 1.1 | [1.2] | 4.130 | 2.86 (3.17) | 5.24 (7.13) | 1.51 (2.18) | 0.24 | e | 0.40 |
| | | ≤0.10 | [2.3] | 3.680 | 4.88 (6.12) | 7.09 f | 2.13 f | 0.59 | 1.31 | 0.75 |
| | | ~0.02 | [2.3] | 3.466 | 6.35 (8.51) | 5.01 f | 2.03 f | 0.91 | 1.55 | 1.18 |
| 1271 | 28.1 | 19.9 | 3.0 | 4.376 | - | - | - | - | - | - |
| | | 16.8 | [5.6] | 3.994 | 2.75 (3.03) | 4.16 (5.58) | 0.77 (1.09) | 0.40 | 0.80 | 0.26 |
| | | 13.2 | [9.5] | 3.396 | 4.91 (6.45) | 7.37 (15.9) | 1.46 (3.57) | 1.18 | 2.65 | 0.86 |
| | | 12.0 | [11.3] | 3.059 | 5.69 (8.36) | 8.11 (22.9) | 1.75 (5.78) | 1.74 | 3.42 | 1.31 |
| 1273 | 27.6 | 23.2 | 0.50 | 4.637 | - | - | - | - | - | - |
| | | 18.2 | [4.4] | 4.225 | 2.86 (3.16) | 4.75 (6.42) | 0.54 (0.77) | 0.45 | 1.69 | 0.51 |
| | | 14.0 | [8.9] | 3.563 | 5.49 (7.29) | 9.37 (20.7) | 2.18 (5.48) | 0.91 | 3.66 | 0.99 |
| | | 13.0 | [10.8] | 3.194 | 6.49 (9.68) | 9.22 (27.0) | 2.16 (7.41) | 1.23 | 4.07 | 1.34 |

Table V-2 (continued) - 3

| ITC Run # | 10 ⁻¹³ x Concentration | | | | 10 ⁻¹¹ x Concentration | | | | | |
|--------------|-----------------------------------|------|-----------------|-------------------|-----------------------------------|-------------|--------------|----------------------------------|-----------------|-----------------|
| | CH ₃ ONO ^a | NO | NO ₂ | Toluene | Benzaldehyde | o-Cresol | m + p-Cresol | Benzyl Nitrate + o-Nitro-toluene | m-Nitro-toluene | p-Nitro-toluene |
| 6-V | 1274 | 25.9 | 12.2 | 36 ^a | 4.382 | - | - | - | - | - |
| | | | 16.4 | [32] ^g | 4.263 | 1.50 (1.55) | 1.49 (1.63) | 0.21 (0.23) | e | 1.10 |
| | | | 21.8 | [26] ^g | 3.998 | 2.72 (3.00) | 5.26 (7.09) | 1.46 (2.08) | 0.43 | 3.29 |
| | | | [24] | [24] ^g | 3.822 | 3.11 (3.60) | 5.93 (9.16) | 0.64 (1.07) | 0.51 | 3.66 |
| | 1275 | 25.2 | 23.0 | 24 ^a | 4.510 | - | - | - | - | - |
| | | | [24] | [23] | 4.263 | 2.08 (2.21) | 4.29 (5.17) | 1.03 (1.29) | 0.21 | 1.85 |
| | | | [24] | [23] | 3.998 | 3.33 (3.79) | 7.55 (11.1) | 1.95 (3.07) | 0.64 | 3.53 |
| | | | [24] | [22] | 3.778 | 4.22 (5.11) | 8.80 (15.3) | 2.28 (4.36) | 1.10 | 4.36 |
| | 1276 | 25.7 | 20.3 | 1.1 | 4.401 | - | - | - | - | - |
| | | | 16.3 | [4.6] | 3.956 | 2.72 (3.05) | 4.85 (6.83) | 1.08 (1.62) | e | 1.15 |
| | | | 12.7 | [8.4] | 3.351 | 4.94 (6.63) | 7.88 (17.9) | 1.13 (2.93) | e | 3.13 |
| | | | 11.8 | [9.9] | 3.048 | 5.94 (8.81) | 9.27 (26.7) | 2.13 (7.20) | e | 3.42 |
| | 1277 | 23.3 | 9.6 | 0.48 | 4.819 | - | - | - | - | - |
| | | | 7.2 | [2.6] | 4.331 | 3.02 (3.39) | 5.54 (7.80) | 1.10 (1.65) | 0.43 | 0.88 |
| | | | 4.3 | [5.8] | 3.670 | 4.96 (6.66) | 7.57 (17.2) | 1.10 (2.85) | 0.94 | 2.14 |
| | | | 2.9 | [7.6] | 3.254 | 6.30 (9.61) | 9.42 (29.0) | 1.51 (5.47) | 1.39 | 3.24 |
| | 1278 | 2.4 | 2.8 | ~0 ^a | 4.628 | - | - | - | - | - |
| | | | 1.2 | [1.4] | 4.132 | 3.49 (3.94) | 6.19 (8.90) | 2.28 (3.50) | 0.40 | 0.37 |
| | | | ~0.07 | [2.3] | 3.680 | 5.13 (6.57) | 7.19 f | 2.72 f | 0.64 | 1.42 |
| | | | ~0.04 | [2.6] | 3.396 | 6.13 (8.55) | 3.21 f | 1.28 f | 0.96 | 1.39 |
| 1279 | 26.6 | 26.6 | 24 ^a | 24 ^a | 4.605 | - | - | - | - | - |
| | | | [25] | [23] | 4.380 | 2.44 (2.58) | 4.39 (5.18) | 1.08 (1.32) | 0.48 | 2.22 |
| | | | [25] | [23] | 4.096 | 4.44 (5.04) | 7.68 (11.2) | 2.10 (3.28) | 0.96 | 4.31 |
| | | | [25] | [23] | 3.892 | 5.16 (6.19) | 8.78 (14.9) | 2.52 (4.69) | 0.83 | 4.52 |

Table V-2 (continued) - 4

| ITC Run # | 10 ⁻¹³ x Concentration | | | | 10 ⁻¹¹ x Concentration | | | | | |
|--------------|-----------------------------------|-------------------|-------------------|---------|-----------------------------------|--------------|--------------|----------------------------------|-----------------|-----------------|
| | CH ₃ ONO ^a | NO | NO ₂ | Toluene | Benzaldehyde | o-Cresol | m + p-Cresol | Benzyl Nitrate + o-Nitro-toluene | m-Nitro-toluene | p-Nitro-toluene |
| 1282 | 5.0 | 2.4 | 2.6 | 4.671 | - | - | - | - | - | - |
| | | 1.2 | [3.7] | 4.208 | 2.91 (3.26) | 6.06 (8.48) | 1.69 (2.51) | 0.37 | 1.20 | 0.45 |
| | | 0.05 | [4.6] | 3.725 | 5.24 (6.69) | 8.24 f | 2.95 f | 0.72 | 2.41 | 0.86 |
| | | -0.02 | [4.8] | 3.426 | 6.13 (8.56) | 5.90 f | 2.10 f | 0.94 | 3.00 | 1.31 |
| 1283 | 5.3 | 5.0 | 0.3 | 4.698 | - | - | - | - | - | - |
| | | 3.1 | [2.1] | 4.145 | 3.55 (4.06) | 6.26 (9.35) | 1.93 (3.10) | 0.45 | 0.43 | 0.29 |
| | | 1.9 | [3.2] | 3.852 | 5.02 (6.21) | 8.57 (15.8) | 2.57 (5.28) | 0.48 | 1.69 | 0.78 |
| | | 0.58 | [4.5] | 3.421 | 6.02 (8.47) | 9.47 (24.1) | 3.00 (8.85) | 0.96 | 2.86 | 1.12 |
| 1284 | 25.4 | 12.0 | 12 ^a | 4.495 | - | - | - | - | - | - |
| | | 11.5 | [12.7] | 4.077 | 3.27 (3.63) | 6.08 (8.33) | 1.85 (2.69) | 0.43 | 2.30 | 0.64 |
| | | 10.7 | [13.8] | 3.784 | 4.85 (5.84) | 8.83 (15.1) | 2.23 (4.20) | 1.04 | 3.00 | 0.80 |
| | | 10.1 | [14.4] | 3.328 | 6.16 (8.51) | 10.04 (24.5) | 2.57 (7.23) | 1.10 | 3.93 | 1.04 |
| 1285 | 25.4 | [37] ^h | [11] ^h | 4.374 | - | - | - | - | - | - |
| | | [35] | [13] | 4.121 | 2.11 (2.25) | 3.72 (4.52) | 0.85 (1.07) | 0.48 | 0.96 | 0.48 |
| | | [30] | [18] | 3.778 | 3.88 (4.54) | 6.62 (10.5) | 1.57 (2.71) | 1.18 | 2.78 | 0.86 |
| | | [28] | [20] | 3.538 | 4.77 (5.99) | 7.57 (14.5) | 1.67 (3.58) | 1.44 | 3.40 | 1.07 |

^aBased on the amounts introduced into the chamber.

^bNo NO or initial NO₂ concentration data; estimated based upon data for analogous run ITC-1263.

^cValues in () are corrected for reaction with the OH radical (see text).

^dValues in [] estimated from computer calculations and NO and/or toluene data.

^eNo data obtained.

^fNO₂ radical reaction contributing to cresol reaction; correction cannot be made.

^gEstimated from measured NO concentrations assuming that ([NO] + [NO₂]) = constant (see text).

^hInitial concentration calculated from the amounts introduced into the chamber, taking into account the dark oxidation of NO to NO₂ during the time between NO injection and the beginning of the irradiation.

Table V-3. Reactant and Product Concentrations (molecule cm^{-3}) During Irradiation of $\text{CH}_3\text{ONO-NO-NO}_2\text{-o-Xylene-Air}$ Mixtures

| ITC Run # | 10^{-13} x Concentration | | | | 10^{-11} x Concentration | | | | | |
|--------------|----------------------------|-------------|---------------|-------------------|---------------------------------------|-----------------------------|-----------------------------|---------------------------------|----------------------|----------------------|
| | CH_3ONO | NO | NO_2 | o-Xylene | o-Tolu- aldehyde | 2,3- Dimethyl- phenol | 3,4- Dimethyl- phenol | 2-Methyl- benzyl- nitrate | 3-Nitro- o-xylene | 4-Nitro- o-xylene |
| V-11 | 1401 | 27.1 | 24^a | 0^a | - | - | - | - | - | - |
| | | | 19.2^b | $[4.8]^c$ | 2.414 | $0.76 (1.16)$ | $0.42 (0.64)$ | 0.49 | 0.45 | 0.45 |
| | | | 16.1^b | $[7.9]$ | $3.58 (4.63)$ | $1.93 (5.38)$ | $1.15 (3.21)$ | 1.40 | 0.72 | 1.70 |
| | | | 14.2^b | $[9.8]$ | 1.593 | $1.99 (7.94)$ | $1.87 (7.46)$ | 1.61 | 0.67 | 2.00 |
| | 1402 | 23.3 | 24^a | 0^a | - | - | - | - | - | - |
| | | | 19.2^b | $[4.8]$ | 2.215 | $0.72 (1.16)$ | $0.34 (0.55)$ | 0.27 | 0.34 | 0.36 |
| | | | 16.1^b | $[7.9]$ | 1.863 | $1.68 (4.16)$ | $0.87 (2.15)$ | 1.22 | 0.63 | 1.55 |
| | | | 14.2^b | $[9.8]$ | 1.612 | $2.07 (7.04)$ | $1.62 (5.51)$ | 1.60 | 0.64 | 1.74 |
| | 1403 | 28.9 | 24^a | 0^a | - | - | - | - | - | - |
| | | | 14.2^b | $[9.8]$ | 1.534 | $2.13 (8.15)$ | $1.42 (5.43)$ | 1.69 | 0.51 | 1.82 |
| | 1404 | 26.9 | 24.0 | 0^a | - | - | - | - | - | - |
| | | | 19.2 | $[4.8]$ | $1.83 (2.01)$ | $0.79 (1.19)$ | $0.47 (0.71)$ | 0.59 | 0.45 | 0.39 |
| | | | 16.1 | $[7.9]$ | $3.33 (4.35)$ | $1.64 (4.73)$ | $0.98 (2.83)$ | 1.44 | 0.52 | 1.48 |
| | | | 14.2 | $[9.8]$ | 1.465 | $2.57 (10.7)$ | $1.87 (7.75)$ | 1.85 | 0.53 | 1.70 |
| | 1405 | 27.5 | 24^a | 24^a | 0.61 | - | - | - | - | - |
| | | | 24^e | $[24]$ | $2.07 (1.60)$ | $0.84 (1.06)$ | $0.43 (0.54)$ | 0.68 | 0.34 | 0.68 |
| | | | 24^e | $[24]$ | $3.10 (3.13)$ | $4.16 (8.25)$ | $2.35 (4.66)$ | 1.39 | 0.36 | 2.38 |
| | | | 24^e | $[24]$ | 1.884 | f | $3.38 (8.94)$ | 1.59 | 0.31 | 2.36 |
| | 1406 | 5.9 | 2.54 | 2.57 | 0.23 | - | - | - | - | - |
| | | | 1.63 | $[3.48]$ | 2.277 | $0.89 (1.38)$ | $0.60 (0.93)$ | 0.43 | 0.31 | 0.39 |
| | | | 0.22 | $[4.89]$ | 1.893 | 1.12 g | 0.76 g | 0.76 | f | 1.10 |
| | | | <0.01 | $[5.11]$ | 1.614 | 0.58 g | 1.76 g | 1.85 | 0.67 | 1.29 |

Table V-3 (continued) - 2

| ITC Run # | 10 ⁻¹³ x Concentration | | | | 10 ⁻¹¹ x Concentration | | | | | |
|--------------|-----------------------------------|------|-----------------|-------------------|-----------------------------------|-----------------------------|-----------------------------|---------------------------------|----------------------|----------------------|
| | CH ₃ ONO | NO | NO ₂ | o-Xylene | o-Tolu- aldehyde | 2,3- Dimethyl- phenol | 3,4- Dimethyl- phenol | 2-Methyl- benzyl- nitrate | 3-Nitro- o-xylene | 4-Nitro- o-xylene |
| V-12 | 1407 | 11.3 | 4.73 | 4.78 | 2.454 | - | - | - | - | - |
| | | | 3.84 | [5.67] | 2.093 | 2.04 (2.26) | 0.96 (1.50) | 0.62 (0.97) | 0.43 | 0.40 |
| | | | 2.02 | [7.49] | 1.608 | 3.39 (4.46) | 1.40 (4.13) | 1.07 (3.16) | 1.07 | 0.34 |
| | | | 0.98 | [8.53] | 1.346 | 3.56 (5.27) | 2.02 g | 1.64 g | 1.49 | 0.46 |
| | 1408 | 22.9 | 12.8 | 11.3 ^a | 2.530 | 0.36 | - | - | - | - |
| | | | 12.1 | [12.0] | 2.286 | 1.78 (1.56) | 0.78 (1.04) | 0.56 (0.75) | 0.43 | 0.28 |
| | | | 11.3 | [12.8] | 1.882 | 3.29 (3.68) | 1.36 (3.00) | 0.93 (2.05) | 1.16 | 0.34 |
| | | | 10.7 | [13.4] | 1.613 | 3.73 (4.72) | 3.69 (11.5) | 2.18 (6.81) | 1.45 | 0.35 |
| | 1409 | 2.3 | 2.33 | 0.22 | 2.417 | - | - | - | - | - |
| | | | 1.15 | [1.40] | 2.085 | 1.86 (2.04) | 0.51 (0.77) | 0.38 (0.57) | 0.37 | 0.16 |
| | | | 0.05 | [2.50] | 1.772 | 2.97 (3.63) | 0.68 g | 0.38 g | 0.67 | 0.65 |
| | | | <0.01 | [2.55] | 1.663 | 3.46 (4.40) | 0.23 g | f | 0.66 | f |
| | 1410 | 5.3 | 5.14 | 0.34 | 2.639 | - | - | - | - | - |
| | | | 3.60 | [1.88] | 2.262 | 2.20 (2.43) | 0.62 (0.96) | 0.37 (0.57) | 0.46 | f |
| | | | 1.51 | [3.97] | 1.807 | 3.61 (4.61) | 1.11 (2.97) | 0.80 (2.14) | 0.77 | f |
| | | | 0.26 | [5.22] | 1.506 | 3.87 (5.58) | 1.00 g | 0.93 g | 1.10 | 0.90 |
| | 1411 | 26.4 | 24 ^a | 0 ^a | 2.735 | 0.23 | - | - | - | - |
| | | | 24.0 | [0] | 2.376 | 2.02 (2.00) | 0.89 (1.32) | 0.64 (0.95) | 0.56 | 0.41 |
| | | | 20.2 | [3.8] | 1.945 | 3.39 (4.03) | 1.92 (4.71) | 1.36 (3.34) | 1.55 | 0.45 |
| | | | 17.3 | [6.7] | 1.565 | 3.75 (5.24) | 3.71 (14.5) | 1.76 (6.90) | 1.78 | 0.46 |
| | 1539 | 25.2 | 22.3 | 1.9 ^a | 2.730 | 0.71 | - | - | - | - |
| | | | 19.9 | [4.3] | 2.450 | 2.05 (1.52) | 1.37 (1.87) | 0.34 (0.46) | 0.72 | 0.35 |
| | | | 16.2 | [8.0] | 1.922 | 4.43 (4.98) | 2.56 (6.43) | 1.26 (3.16) | 2.63 | 0.67 |
| | | | 13.9 | [10.3] | 1.598 | 4.39 (5.70) | 3.13 (11.7) | 1.46 (5.47) | 3.35 | 0.78 |

Table V-3 (continued) - 3

| ITC Run # | 10 ⁻¹³ x Concentration | | | | 10 ⁻¹¹ x Concentration | | | | | |
|--------------|-----------------------------------|-----------------|-------------------|----------|-----------------------------------|-----------------------------|-----------------------------|---------------------------------|----------------------|----------------------|
| | CH ₃ ONO | NO | NO ₂ | o-Xylene | o-Tolu- aldehyde | 2,3- Dimethyl- phenol | 3,4- Dimethyl- phenol | 2-Methyl- benzyl- nitrate | 3-Nitro- o-xylene | 4-Nitro- o-xylene |
| 1540 | ~24 | 15.4 | 32.6 ^a | 2.832 | 1.24 | f | f | f | f | - |
| | | 21.1 | [26.9] | 2.582 | 2.19 (1.15) | f | f | f | f | 0.75 |
| | | 25 ^e | [23] | 2.251 | 3.57 (3.06) | f | f | f | f | 2.92 |
| | | 25 ^e | [23] | 2.009 | 4.61 (4.75) | f | f | f | f | 2.84 |
| 1541 | 24.8 | 22.0 | 26.0 ^a | 2.668 | 1.75 | 0.55 | - | - | - | - |
| | | 25 ^e | [23] | 2.484 | 2.18 (0.61) | 2.10 (2.14) | 0.92 (1.13) | 0.87 | 0.34 | 0.42 |
| | | 25 ^e | [23] | 2.146 | 4.68 (3.85) | 4.11 (7.20) | 2.08 (3.78) | 2.52 | 0.67 | 2.56 |
| | | 25 ^e | [23] | 1.886 | 3.72 (3.23) | 3.16 (7.68) | 1.50 (3.73) | 2.53 | 0.48 | 2.47 |
| 1542 | 24.9 | 11.6 | 11.6 ^a | 2.548 | 0.87 | - | - | 0.23 | - | - |
| | | 11.2 | [12.0] | 2.273 | 2.36 (1.73) | 1.72 (2.38) | 0.72 (1.00) | 0.83 | 0.37 | 0.36 |
| | | 10.0 | [13.2] | 1.831 | 3.93 (4.16) | 3.11 (7.43) | 1.63 (3.90) | 2.13 | 0.48 | 2.25 |
| | | 9.17 | [14.0] | 1.519 | 4.41 (5.54) | 3.04 (11.0) | 1.49 (5.37) | 2.43 | 0.56 | 2.07 |
| 1543 | 5.1 | 2.26 | 2.38 | 2.497 | 0.46 | - | - | - | - | - |
| | | 1.46 | [3.18] | 2.182 | 2.03 (1.78) | 1.10 (1.61) | 0.52 (0.76) | 0.83 | 0.22 | 0.31 |
| | | 0.14 | [4.50] | 1.783 | 3.69 (4.20) | 1.63 g | 0.94 g | 1.65 | 0.41 | 1.07 |
| | | 0.06 | [4.58] | 1.574 | 3.64 (4.55) | 1.25 g | 0.72 g | 2.03 | 0.48 | 1.07 |

^aBased upon amounts introduced into the chamber.^bBy analogy with run ITC-1404.^cValues in [] are the NO₂ concentrations estimated from the NO data, assuming that ([NO] + [NO₂]) = constant (see text).^dValues in () are the amounts formed in the reactions, corrected for reaction with the OH radical (see text).^eEstimated from computer modeling of analogous irradiated CH₃ONO-NO-NO₂-toluene-air mixtures.^fNo data obtained.^gNO₃ radical reactions also contributing to dimethylphenol loss; corrections cannot be made.

Table V-4. Reactant and Product Concentrations (molecule cm^{-3}) During Irradiation of $\text{CH}_3\text{ONO-NO-NO}_2\text{-m-Xylene-Air}$ Mixtures

| ITC Run # | 10^{-13} x Concentration | | | | 10^{-11} x Concentration | | | | | |
|--------------|----------------------------|-----------------|--------------------|----------|----------------------------|-----------------------------|-----------------------------|---------------------------------|----------------------|----------------------|
| | CH_3ONO | NO | NO_2 | m-Xylene | m-Tolu- aldehyde | 2,6- Dimethyl- phenol | 2,4- Dimethyl- phenol | 3-Methyl- benzyl- nitrate | 4-Nitro- m-xylene | 5-Nitro- m-xylene |
| 1567 | 25.7 | 23.2 | 0.8 ^a | 3.103 | - | - | - | - | - | - |
| | | 21.1 | [2.9] ^b | 2.755 | 1.51 (1.58) ^c | 2.06 (2.43) | 1.58 (1.89) | d | d | d |
| | | 17.6 | [6.4] | 2.201 | 3.00 (3.42) | 4.27 (6.82) | 3.70 (6.13) | 0.53 | d | 0.52 |
| | | 15.2 | [8.8] | 1.812 | 3.58 (4.41) | 5.28 (10.9) | 4.75 (10.3) | 0.89 | 0.25 | 0.54 |
| 1568 | 24.6 | 21.8 | 26.2 ^a | 3.071 | 0.58 | 1.56 | - | - | - | - |
| | | 24 ^e | [24] | 2.844 | 1.70 (1.18) | 2.74 (1.31) | 1.70 (1.91) | d | d | 0.32 |
| | | 24 ^e | [24] | 2.419 | 2.64 (2.35) | 6.05 (6.23) | 4.46 (6.35) | 0.36 | d | 0.55 |
| | | 25 ^e | [23] | 2.165 | 3.31 (3.26) | 7.63 (9.77) | 5.33 (8.91) | 0.68 | 0.24 | 0.76 |
| 1570 | 25.0 | 13.6 | 12.0 ^a | 3.482 | 0.70 | - | - | - | - | - |
| | | 13.2 | [12.4] | 3.168 | 1.56 (0.94) | 2.86 (3.26) | 2.62 (3.02) | 0.40 | d | 0.39 |
| | | 12.2 | [13.4] | 2.635 | 3.55 (3.31) | 6.53 (9.56) | 5.42 (8.18) | 0.36 | d | 0.59 |
| | | 11.4 | [14.2] | 2.239 | 4.03 (4.17) | 8.45 (15.4) | 7.01 (13.4) | 0.63 | d | 0.61 |
| 1571 | 2.5 | 2.26 | 0.21 | 3.132 | 0.61 | 0.49 | - | - | - | - |
| | | 1.66 | [0.81] | 2.772 | 1.85 (1.35) | 1.42 (1.27) | 1.57 (1.87) | d | d | d |
| | | 0.50 | [1.97] | 2.266 | 3.07 (2.93) | 2.45 (3.50) | 3.07 (4.95) | 0.48 | 0.11 | d |
| | | 0.11 | [2.36] | 2.033 | 3.62 (3.75) | 3.29 ^f | 3.50 ^f | 0.76 | 0.24 | 0.39 |
| 1572 | 27.2 | 17.4 | 18.2 ^a | 2.953 | 0.72 | - | - | - | - | - |
| | | 17.8 | [17.8] | 2.664 | 1.85 (1.23) | 2.98 (3.44) | 2.11 (2.46) | 0.12 | d | 0.27 |
| | | 17.6 | [18.0] | 2.182 | 2.95 (2.66) | 6.60 (9.98) | 5.45 (8.52) | 0.97 | 0.34 | 0.86 |
| | | 17.4 | [18.2] | 1.836 | 3.79 (3.94) | 7.82 (14.9) | 6.36 (12.7) | 0.70 | 0.11 | 0.50 |

^aBased on amount introduced into chamber.

^bValues in [] are the NO_2 concentrations estimated from the NO data, assuming that $([\text{NO}] + [\text{NO}_2]) = \text{constant}$ (see text).

^cValues in () are the amounts formed in the reactions, corrected for reaction with the OH radical (see text).

^dNo data obtained.

^eEstimated from computer modeling of analogous irradiated $\text{CH}_3\text{ONO-NO-NO}_2\text{-toluene-air}$ mixtures.

^f NO_3 radical reactions also contributing to dimethylphenol loss; corrections cannot be made.

Table V-5. Reactant and Product Concentrations (molecule cm^{-3}) During Irradiation of $\text{CH}_3\text{ONO-NO-NO}_2$ -p-Xylene-Air Mixtures

| ITC Run # | 10^{-13} x Concentration | | | | 10^{-11} x Concentration | | | |
|--------------|----------------------------|-------------|-----------------|--------------------|----------------------------|--------------------------|----------------------------|------------------|
| | CH_3ONO | NO | NO_2 | p-Xylene | p-Tolualdehyde | 2,5-Dimethyl- phenol | 4-Methylbenzyl- Nitrate | 2-Nitro-p-xylene |
| V-15 | 1560 | 25.0 | 24 ^a | 0 ^a | 2.642 | - | - | - |
| | | | 20.0 | [4.0] ^b | 2.359 | 2.42 (2.60) ^c | 0.86 | 0.58 |
| | | | 16.1 | [7.9] | 1.829 | 5.10 (6.41) | 1.18 | 1.51 |
| | | | 13.6 | [10.4] | 1.522 | 5.83 (8.24) | 1.07 | 1.91 |
| | 1561 | 27.8 | 24 ^a | 24 ^a | 3.224 | 0.46 | - | - |
| | | | 24 ^d | [24] | 2.952 | 3.26 (3.01) | 1.11 | 0.83 |
| | | | 24 ^d | [24] | 2.438 | 5.95 (6.68) | 1.32 | 1.82 |
| | | | 24 ^d | [24] | 2.131 | 6.98 (8.66) | 1.20 | 2.04 |
| | 1562 | 3.3 | 2.76 | 0.84 | 3.280 | 0.17 | - | - |
| | | | 1.13 | [2.47] | 2.676 | 3.24 (3.52) | 0.55 | 0.55 |
| | | | 0.10 | [3.50] | 2.244 | 6.58 (8.19) | 0.99 | 1.22 |
| | | | 0.01 | [3.59] | 1.982 | 6.58 (8.89) | 1.92 e | f |
| | 1563 | 25.3 | 12.4 | 12.0 ^a | 3.121 | 0.38 | - | - |
| | | | 12.1 | [12.3] | 2.786 | 2.90 (2.75) | 4.39 (5.96) | 1.16 |
| | | | 11.2 | [13.2] | 2.249 | 5.81 (6.79) | 8.18 (18.7) | 1.69 |
| | | | 10.6 | [13.8] | 1.896 | 6.43 (8.50) | 6.91 (22.8) | 1.05 |
| | 1565 | 2.6 | 2.11 | 0.24 | 2.922 | - | - | - |
| | | | 1.14 | [1.21] | 2.482 | 2.78 (3.07) | 2.90 (4.48) | 0.43 |
| | | | 0.11 | [2.24] | 2.090 | 5.47 (6.73) | 3.72 e | 0.78 |
| | | | 0.02 | [2.33] | 1.879 | 5.69 (7.49) | 1.94 e | 0.67 |

^aBased on amount introduced into chamber.

^bValues in [] are calculated assuming $([\text{NO}] + [\text{NO}_2]) = \text{constant}$.

^cValues in () are the amounts formed in the reactions, corrected for reaction with the OH radical (see text).

^dEstimated from computer modeling of analogous irradiated $\text{CH}_3\text{ONO-NO-NO}_2$ -toluene-air mixtures.

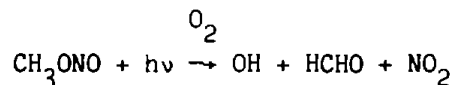
^e NO_3 radical reactions also contributing to dimethylphenol loss; corrections cannot be made (see text).

^fNo data obtained.

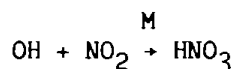
+ p-cresol, benzyl nitrate + o-nitrotoluene (assuming equal FID responses for benzyl nitrate and o-nitrotoluene), m-nitrotoluene and p-nitrotoluene during the $\text{CH}_3\text{ONO-NO-NO}_2$ -toluene-air irradiations are given in Table V-2.

The observed concentrations of NO, xylene, tolualdehyde, dimethylphenol(s), nitro-xylene(s) and methylbenzyl nitrate (assuming equal FID responses for the methylbenzyl nitrates and the nitro-xylenes) during the $\text{CH}_3\text{ONO-NO-NO}_2$ -xylene-air irradiations are given in Tables V-3 through V-5. In the p-xylene system, the 2-nitro-p-xylene and 4-methylbenzyl nitrate were only partially resolved on the DB-5 megabore column used for the GC-FID analyses, and hence the concentrations of these individual products given in Table III are subject to significant uncertainties (the sum of the concentrations of these products is more precise).

As noted in the Experimental section above, only the NO_2 concentrations prior to the addition of CH_3ONO could be measured, and total oxides of nitrogen concentrations $>2.4 \times 10^{14}$ molecule cm^{-3} could not be measured. The initial CH_3ONO and, in some cases, the initial NO and/or NO_2 concentrations were calculated from the amounts of NO, NO_2 and CH_3ONO introduced into the chamber and the known volume of the chamber. The computer calculations showed that to a very good approximation the sum of the NO and the NO_2 concentrations in irradiated $\text{CH}_3\text{ONO-NO-NO}_2$ -organic-air mixtures remains constant. This finding is consistent with OH radical formation from the overall photooxidation of CH_3ONO



being balanced by OH radical removal, predominantly with NO_2 ,



and with the OH radical reactions with the organic compounds present leading to the conversion of NO to NO_2 . The measured or estimated NO and NO_2 concentrations during the $\text{CH}_3\text{ONO-NO-NO}_2$ -air irradiations are also given in Tables V-1 through V-5.

The products formed from these OH radical-initiated reactions can also be removed by reaction, but, providing that the product species only reacted with the OH radical, the measured concentrations can readily be corrected to take into account these losses, as described in detail previously (Atkinson et al., 1982b). For benzaldehyde, the tolualdehydes, phenol, the cresols, and the dimethylphenols, other loss processes must also be considered in addition to the OH radical reaction. Thus, benzaldehyde (and presumably also the tolualdehydes) also photolyzes (see Atkinson and Lloyd, 1984) but, at the OH radical concentrations in these irradiations $[(0.4-2) \times 10^8 \text{ molecule cm}^{-3}]$ averaged over the duration of the irradiations, as calculated from the aromatic hydrocarbon time-concentration profiles, the OH radical reaction was calculated to be the dominant loss process. Phenol, the cresols and the dimethylphenols also react rapidly with the NO_3 radical (Atkinson et al., 1984, 1988), and this reactive loss process was shown from the computer calculations to become important under conditions where the NO_2/NO concentration ratio exceeded $\sim 7-8$. Thus, for the longer irradiation times in the benzene runs ITC-1295 and 1296, the toluene runs ITC-1268, 1269, 1270, 1278 and 1282, the o-xylene runs ITC-1406, 1407, 1409, 1410 and 1543, the m-xylene run ITC-1571 and the p-xylene runs ITC-1562 and 1565, the NO_3 radical reactions were calculated to contribute $\geq 10\%$ of the overall removal rates of phenol, the cresols, or the dimethylphenols, and these data were not used in the determination of the formation yields of these products. The occurrence of these NO_3 radical reactions in these irradiations was confirmed by the decrease in the measured phenol, cresol or dimethylphenol concentrations with increasing irradiation time. For all other runs, the dominant phenol, cresol or dimethylphenol removal process throughout the irradiation was by reaction with the OH radical. The OH radical rate constants at 298 K used to take into account product removal by OH radical reaction were (in units of $10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$): benzene, 1.23; phenol, 26.3; nitrobenzene, 0.14; toluene, 5.96; benzaldehyde, 12.9; o-cresol, 40; m- + p-cresol, 48; o-nitrotoluene, 0.70; m-nitrotoluene, 0.95; o-xylene, 13.7; m-xylene, 23.6; p-xylene, 14.3; o-, m- and p-tolualdehyde, each 17.3; 2,3-dimethylphenol, 80.2; 3,4-dimethylphenol, 81.4; 2,4-dimethylphenol, 71.5; 2,6-dimethylphenol, 65.9; 2,5-dimethylphenol, 80.0; 3- and 4-nitro-o-xylene and 2-nitro-p-xylene, each ~ 2.1 ; 4-nitro-m-xylene, ~ 3.0 ; 5-nitro-m-xylene, ~ 1.9 ; and methylbenzyl nitrates ≤ 5 .

Use of these OH radical reaction rate constants allowed the observed product concentrations during the irradiations to be corrected to take into account the losses of the products by OH radical reaction, and the corrected concentrations are given in Tables V-1 through V-5.

In addition to the experiments described above, several control experiments were carried out. Irradiation of a m-nitrotoluene (8.6×10^{12} molecule cm^{-3})-NO(2.4×10^{14} molecule cm^{-3})-air mixture for 10 min at the maximum light intensity resulted in <10% loss of the m-nitrotoluene, showing that any photolysis of the nitrotoluene was of negligible importance. The observation that photolysis of m-nitrotoluene was not important is consistent with our previous data for nitrobenzene (Atkinson et al., 1985). Irradiation of a toluene (4.8×10^{13} molecule cm^{-3})-NO (2.4×10^{14} molecule cm^{-3})-air mixture gave rise to no observable products by GC analysis. An experiment was also carried out in which 2.4×10^{14} molecule cm^{-3} each of NO and NO₂ were introduced into the chamber together with o-cresol, and samples taken for GC analyses from this reaction mixture in the dark and after irradiation for 3 min at the maximum light intensity. Products were observed both in the dark and after irradiation which were tentatively identified as being nitrocresols (having the same GC retention times as those products formed after prolonged irradiation of CH₃ONO-NO-NO₂-toluene-air mixtures). None of the nitrotoluenes were observed from this o-cresol-NO-NO₂-air reaction mixture, either in the dark or after irradiation. These control experiments indicate that the products for which data are given in Tables V-1 through V-5 were formed as products of the gas-phase reaction of the OH radical with benzene or toluene, in the presence of NO_x.

The product data given in Tables V-1 through V-5 are evaluated in the following sections. Since a more extensive study was carried out for toluene (22 irradiations) than for benzene (10 irradiations), o-xylene (16 irradiations), m-xylene (5 irradiations) or p-xylene (5 irradiations), the toluene data are dealt with first.

Toluene. The data given in Table V-2 for the yields of benzaldehyde, o-cresol and m- + p-cresol (corrected to take into account losses whenever these were solely due to reaction with the OH radical) do not show any obvious dependence on the NO or NO₂ concentrations during the irradiations. Plots of the amounts of these products formed, corrected for OH

radical reaction, against the amount of toluene reacted are shown in Figures V-1 (benzaldehyde) and V-2 (o-cresol and m- + p-cresol). Within the scatter of the data, these plots are reasonably straight lines, indicating (especially for the cresols which have high correction factors) that the correction factors to take into account OH radical reaction of these products were appropriate. Least-squares analyses of the data given in Table V-2 and shown in Figures V-1 and V-2 lead to benzaldehyde and cresol formation yields of: benzaldehyde, 0.0645 ± 0.0033 ; o-cresol, 0.204 ± 0.014 ; and m- + p-cresol, 0.048 ± 0.007 . Inclusion of the estimated overall uncertainties in the toluene and product GC-FID calibration factors, of $\pm 5\%$ and $\pm 10\%$, respectively, leads to formation yields of benzaldehyde, 0.0645 ± 0.0080 ; o-cresol, 0.204 ± 0.027 ; and m- + p-cresol, 0.048 ± 0.009 .

The GC-MS response factors of selected ions of the three nitrotoluene isomers were determined, and GC-MS analysis of an irradiated $\text{CH}_3\text{ONO-NO-NO}_2$ -toluene-air mixture showed the o-nitrotoluene: m-nitrotoluene: p-nitrotoluene product ratio to be 0.07:1.0:0.35. Thus, m-nitrotoluene was the most abundant of the nitrotoluene isomers formed, and the following analysis deals with this isomer. The data given in Table V-2 indicate that the m-nitrotoluene yield depends on the NO_2 concentration during the irradiation, with the yield increasing with increasing average NO_2 concentration (compare runs ITC-1270 and 1278 versus runs ITC-1274, 1275 and 1279). However, as shown by the plot of the amount of m-nitrotoluene formed against the amount of toluene reacted in the analogous runs ITC-1260, 1261, 1263, 1273 and 1276 (Figure V-3), the m-nitrotoluene yield did not increase with the extent of reaction commensurate with the marked increase in the NO_2 concentration with the extent of reaction (also shown in Figure V-3).

To further explore the relationship between the m-nitrotoluene formation yield and the NO_2 concentration, the data given in Table V-2 were analyzed in two ways. In the first approach, the incremental m-nitrotoluene yields $\{(\Delta[\text{m-nitrotoluene}]/\Delta[\text{toluene}])_{t_1-t_2}\}$ have been plotted against the average NO_2 concentrations during these time intervals $[0.5([\text{NO}_2]_{t_1} + [\text{NO}_2]_{t_2})]$, and this plot is shown in Figure V-4B. Despite the (expected) high degree of scatter, the m-nitrotoluene yield appears to increase with the NO_2 concentration, with a non-zero intercept. Least-

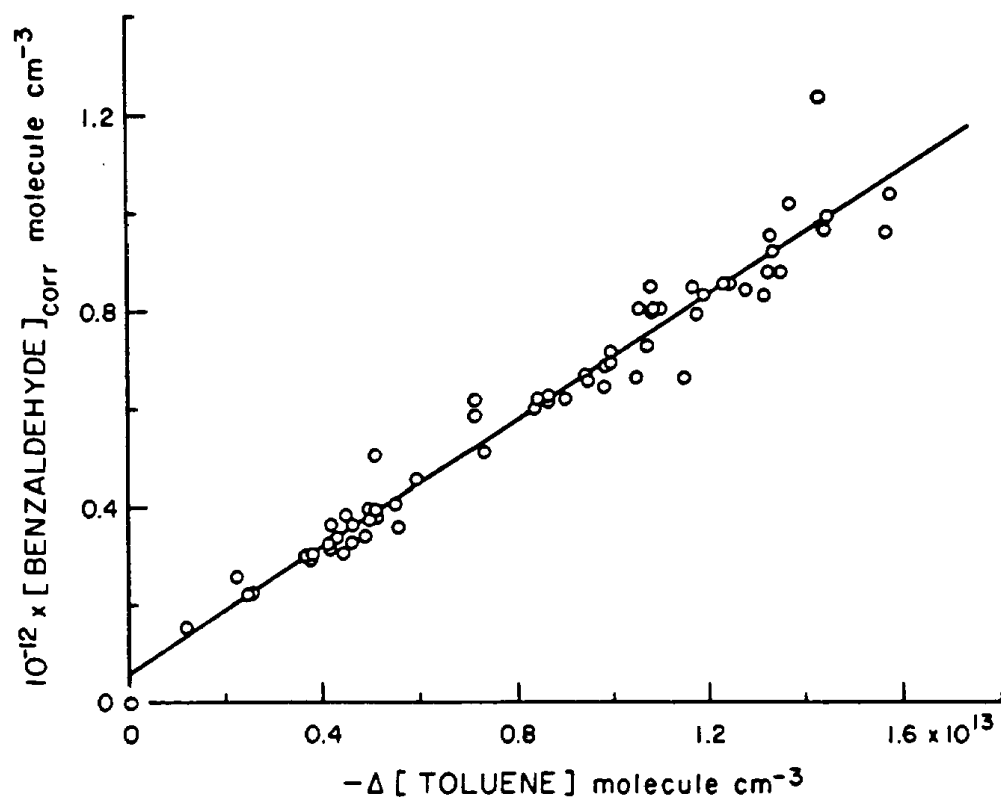


Figure V-1. Plot of the amount of benzaldehyde formed, corrected for reactive loss with the OH radical (see text), against the amount of toluene reacted.

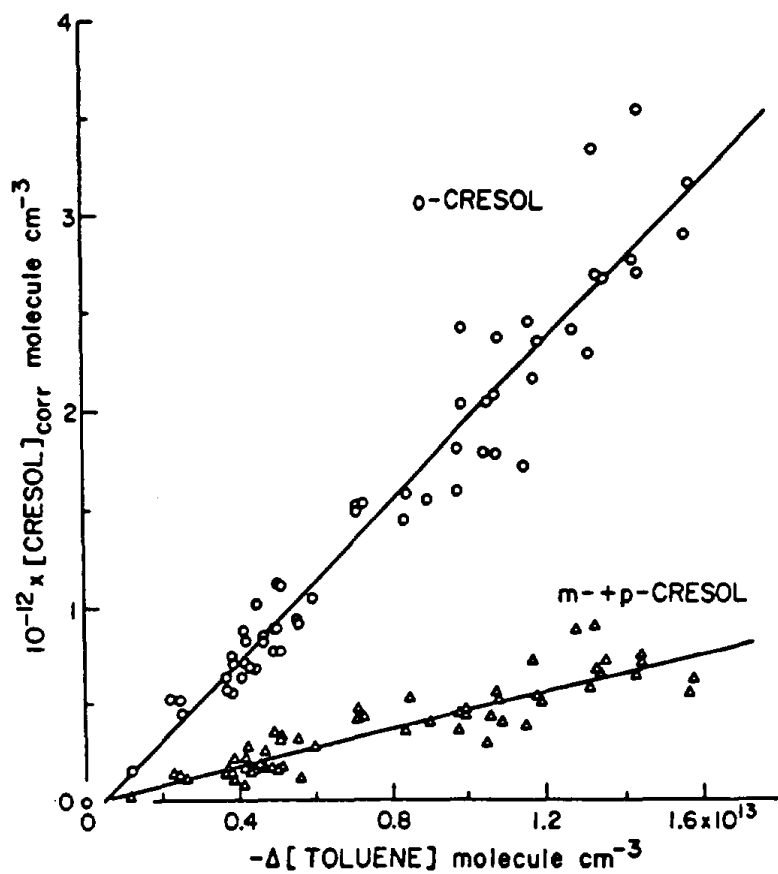


Figure V-2. Plots of the amounts of o-cresol and m- plus p-cresol formed, corrected for reactive loss with the OH radical (see text), against the amount of toluene reacted.

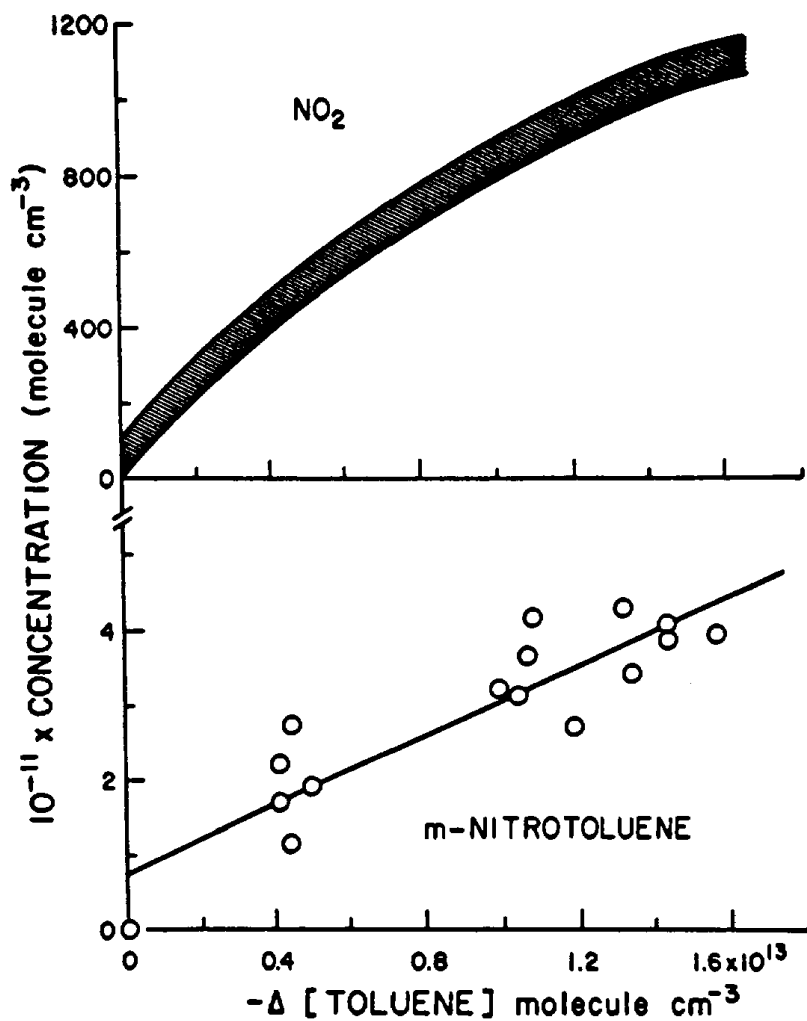


Figure V-3. Plots of the NO_2 (top) and m-nitrotoluene (bottom) concentrations against the amount of toluene reacted for ITC runs 1260, 1261, 1263, 1273 and 1276. The line drawn through the m-nitrotoluene data is the least-squares fit.

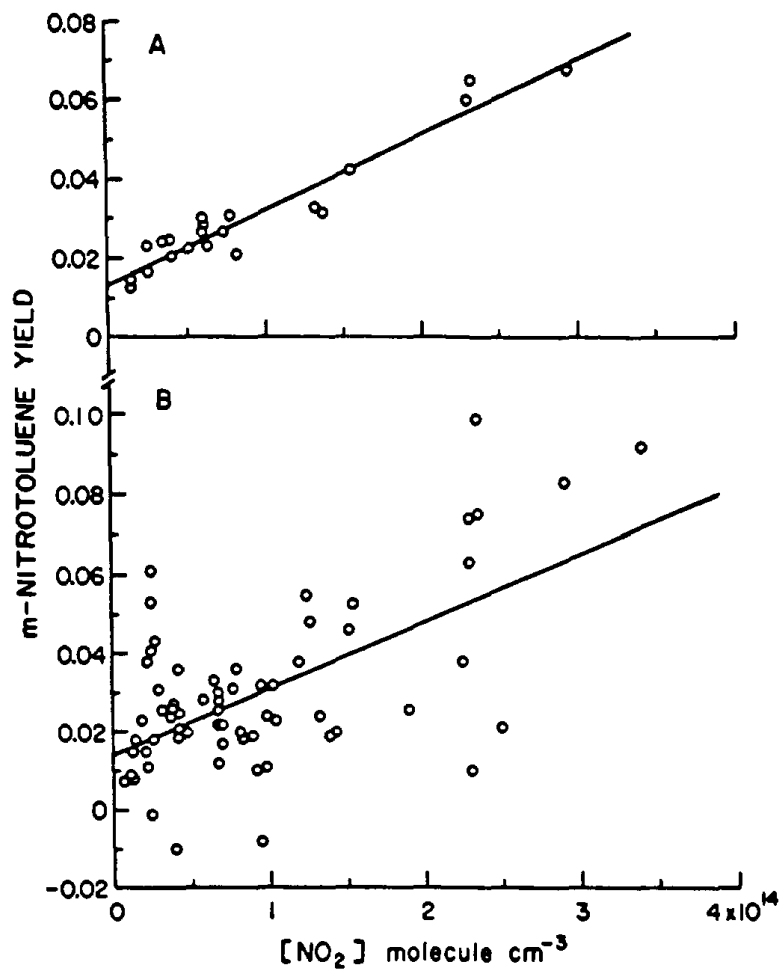


Figure V-4. Plots of the m-nitrotoluene formation yield against the NO_2 concentration. A - averaged data from each irradiation. B - from individual data points (see text).

squares analysis of these data in Figure V-4B yields a slope and intercept of $(1.69 \pm 0.56) \times 10^{-16} \text{ cm}^{-3} \text{ molecule}^{-1}$ and 0.0146 ± 0.0067 , respectively. Since the plots of the amounts of m-nitrotoluene formed during these reactions against the amounts of toluene reacted were reasonably linear (see, for example, Figure V-3), in the second approach the m-nitrotoluene yield for each irradiation (obtained from least-squares analysis of the m-nitrotoluene versus toluene data) was plotted against the mean NO_2 concentration for that irradiation ($[\text{NO}_2]_{\text{av}} = n^{-1} \sum_1^n [\text{NO}_2]_n$), as shown in Figure V-4A. (In most cases the NO_2 concentrations did not vary markedly during the irradiations). As anticipated, due to the "averaging" effect of this analysis, the plot in Figure V-4A is much less scattered than that in Figure V-4B, but also shows that the m-nitrotoluene yield increases reasonably linearly with the NO_2 concentration, and again has a distinct non-zero intercept when extrapolated to zero NO_2 concentration. A least-squares analysis of the data shown in Figure V-4A leads to a slope and intercept of $(1.90 \pm 0.25) \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1}$ and 0.0135 ± 0.0029 , respectively. The slopes and intercepts of the plots shown in Figure V-4A and V-4B are identical within the two standard deviation error limits, and show that while the m-nitrotoluene yield does increase with the NO_2 concentration, it does not extrapolate to zero as the NO_2 concentration approaches zero.

The m- and p-nitrotoluene data given in Table V-2 show that the average p-nitrotoluene: m-nitrotoluene ratio was 0.35, in agreement with the GC-MS value for a single $\text{CH}_3\text{ONO-NO-NO}_2$ -toluene-air irradiation. Within the appreciable scatter in the data, it thus appears that the p-nitrotoluene formation yield (scaled by a factor of 0.35) parallels that for m-nitrotoluene. Assuming that the o-nitrotoluene formation yield is consistently 0.07 that of m-nitrotoluene allows the benzyl nitrate + o-nitrotoluene concentration data (Table V-2) to be corrected for the minor presence of o-nitrotoluene. The benzyl nitrate formation yield is then calculated to be 0.0084 ± 0.0017 , where the indicated error is two least-squares standard deviations and does not take into account any systematic errors arising from uncertainties in the o-nitrotoluene yields or in the GC-FID response factor for benzyl nitrate.

Benzene. The phenol (corrected for reaction with the OH radical) and nitrobenzene data are given in Table V-1. Analogous to the situation for

the cresols, the phenol formation yield appeared to be independent of the NO_2 concentration, and a plot of the phenol concentrations during the $\text{CH}_3\text{ONO-NO-NO}_2$ -benzene-air irradiations (corrected to take into account OH reaction losses) against the amount of benzene reacted is shown in Figure V-5. This plot is a reasonably good straight line, and a least-squares analysis leads to the formation yield of phenol from benzene of 0.236 ± 0.034 . Inclusion of the estimated overall uncertainties in the GC-FID calibration factors for benzene and phenol leads to a yield of 0.236 ± 0.044 .

The nitrobenzene data are analogous to the m-nitrotoluene data from the toluene system in that the formation yield is higher in the irradiations with higher average NO_2 concentrations (compare, for example, runs ITC-1294 and 1295). Figure V-6 shows a plot of the nitrobenzene yields, obtained from the data for each irradiation, against the mean NO_2 concentrations (using data analysis analogous to that shown in Figure V-4A). As for the formation of m-nitrotoluene from toluene, the nitrobenzene formation yield increases with the NO_2 concentration, with a non-zero intercept when extrapolated to zero NO_2 concentration. Least-squares analysis of the data shown in Figure V-6 leads to a slope and intercept of $(3.07 \pm 0.92) \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1}$ and 0.0336 ± 0.0078 , respectively. (Analysis of the data by the method used for Figure V-4B leads to a similar slope and intercept, although with significantly higher uncertainties).

Xylenes. The products observed and quantified from the $\text{CH}_3\text{ONO-NO-NO}_2$ -xylene-air irradiations were: from o-xylene, o-tolualdehyde, 2-methylbenzyl nitrate, 2,3-dimethylphenol, 3,4-dimethylphenol, 3-nitro-o-xylene and 4-nitro-o-xylene; from m-xylene, m-tolualdehyde, 3-methylbenzyl nitrate, 2,4-dimethylphenol, 2,6-dimethylphenol, 4-nitro-m-xylene and 5-nitro-m-xylene; and from p-xylene, p-tolualdehyde, 4-methylbenzyl nitrate, 2,5-dimethylphenol and 2-nitro-p-xylene. Neither 3,5-dimethylphenol nor 2-nitro-m-xylene were observed from the m-xylene reaction system, in agreement with the previous study of Gery et al. (1987).

Within the experimental uncertainties, the data given in Tables V-3 through V-5 for the tolualdehyde and dimethylphenol yields (corrected to take into account losses whenever these were solely due to reaction with the OH radical) do not show any obvious dependence on the NO or NO_2 concentrations during the irradiations. Plots of the amounts of these

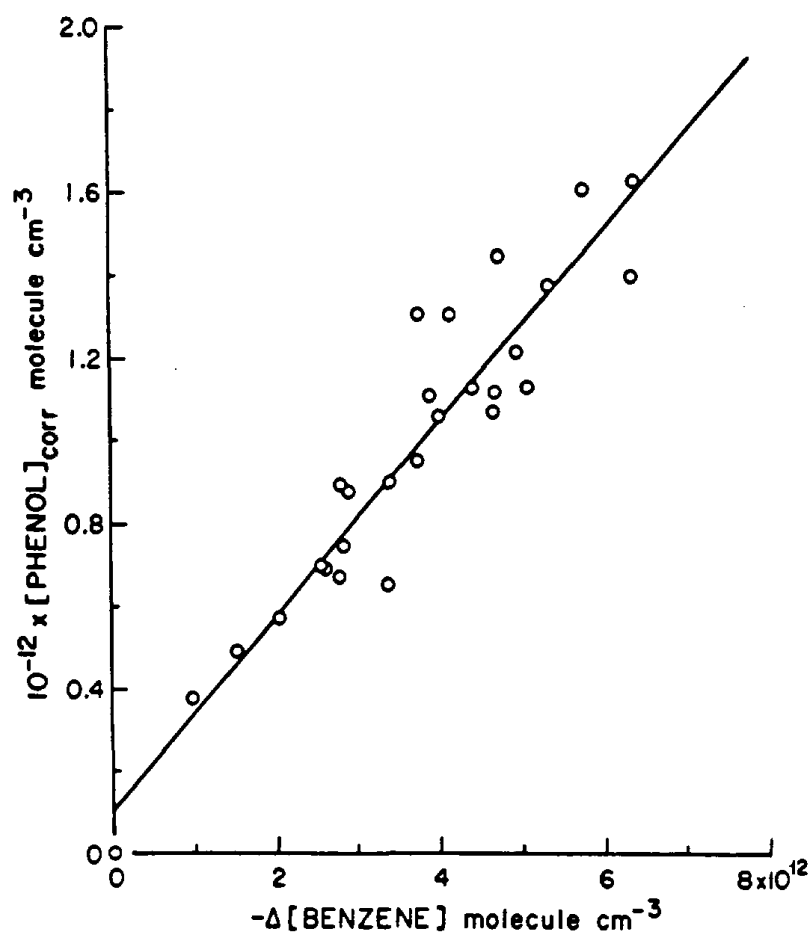


Figure V-5. Plot of the amount of phenol formed, corrected for reactive loss with the OH radical (see text), against the amount of benzene reacted.

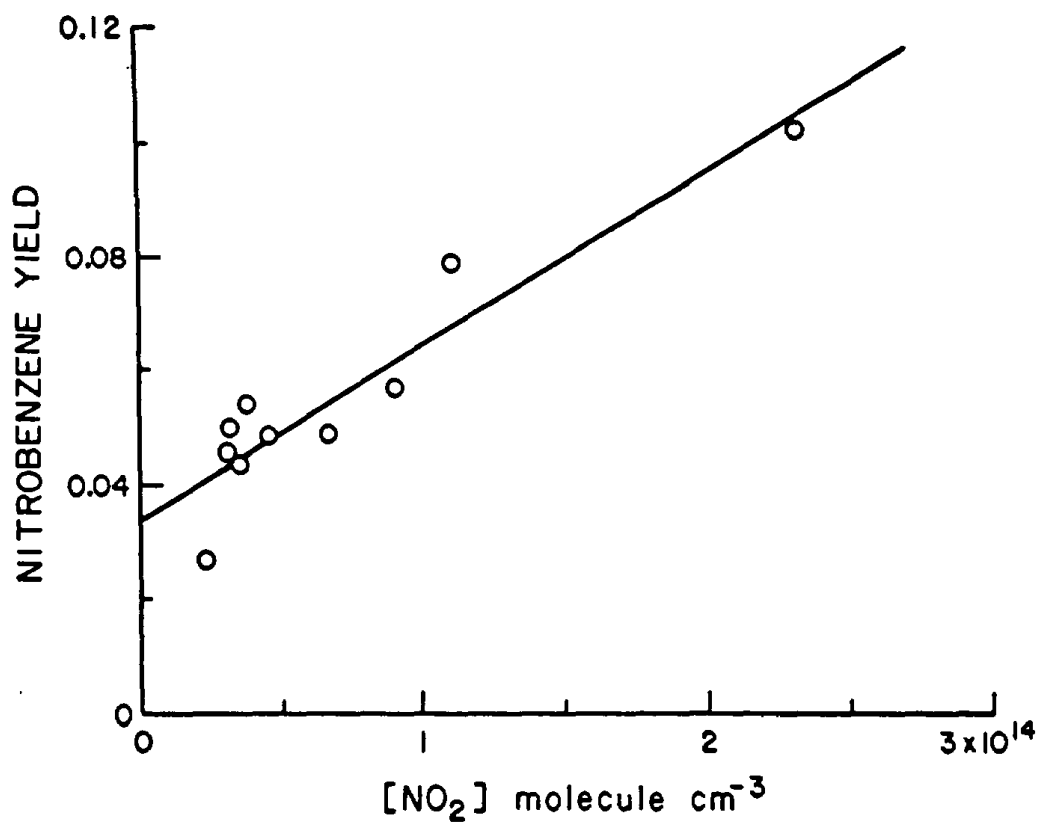


Figure V-6. Plot of the nitrobenzene formation yield against the NO₂ concentration (averaged data from each irradiation).

products formed, corrected for OH radical reaction, against the amounts of o-, m- or p-xylene reacted are shown in Figures V-7 (tolualdehydes) and V-8 (dimethylphenols). Within the scatter of the data, which is appreciable for the dimethylphenols, these plots are reasonable straight lines, and the least-squares formation yields of the tolualdehydes and dimethylphenols from the OH radical-initiated reactions of o-, m- and p-xylene are given in Table V-6.

The amounts of the various methylbenzyl nitrates and nitro-xylenes formed during these irradiated $\text{CH}_3\text{ONO-NO-NO}_2$ -xylene air mixtures were in all cases low, $\leq 3.4 \times 10^{11}$ molecule cm^{-3} for o-xylene, $\leq 1.0 \times 10^{11}$ molecule cm^{-3} for m-xylene and $\leq 2.1 \times 10^{11}$ molecule cm^{-3} for p-xylene. The highest concentrations of the methylbenzyl nitrate and nitro-xylene products were formed in the o-xylene reactions. As observed for the formation of m-nitrotoluene from toluene (Figure V-3), for a given experiment the amount of 4-nitro-o-xylene formed (the most abundant of the two nitro-o-xylenes) increased essentially linearly with the amount of o-xylene reacted, despite the fact that the NO_2 concentration was not always constant. Thus, for example, the amount of 4-nitro-o-xylene formed increased essentially linearly with the amount of o-xylene reacted during the closely similar runs ITC-1401, 1402, 1403, 1404, 1411 and 1539, for which the NO_2 concentrations increased from approximately zero at the beginning of the irradiations to $\sim 1.0 \times 10^{14}$ molecule cm^{-3} at the end of the experiments.

The methylbenzyl nitrate and nitro-xylene yields were determined for each irradiation by least squares analysis of the methylbenzyl nitrate or nitro-xylene versus xylene data. These formation yields of the methylbenzyl nitrates and nitro-xylenes, determined for each irradiation, are plotted against the mean NO_2 concentration for that irradiation ($[\text{NO}_2]_{\text{av}} = n^{-1} \sum_1^n [\text{NO}_2]_n$) in Figures V-9 (methylbenzyl nitrates) and V-10 (nitro-xylenes). The formation yields of these nitrate and nitro-products as given by least-squares analyses of the data shown in Figures VI-9 and V-10 are given in Table V-6.

It should be noted that the amounts of 5-, and especially, 4-nitro-m-xylene formed from m-xylene were low, with complete data sets not being obtained for most of the irradiations (Table V-4), and hence the formation yields of these two nitro-m-xylenes have significant associated

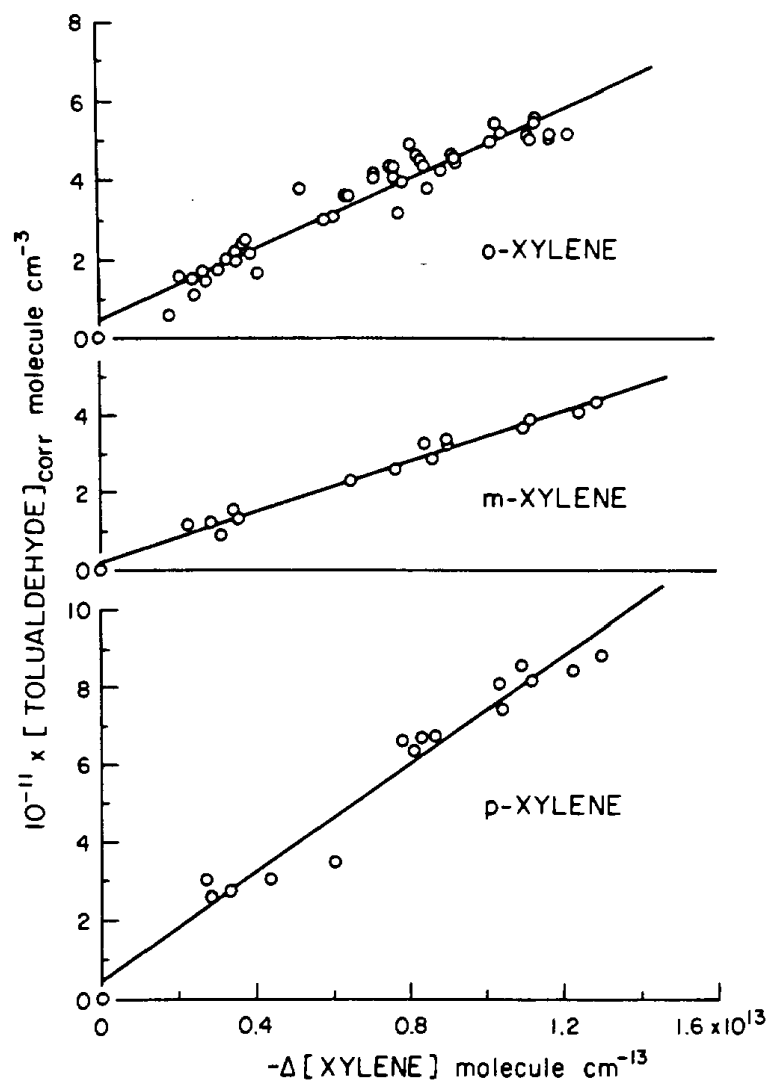


Figure V-7. Plots of the amounts of o-, m- and p-tolualdehyde formed (corrected to take into account reaction with the OH radical, see text) against the amounts of o-, m- and p-xylene, respectively, reacted in irradiated $\text{CH}_3\text{ONO-NO-NO}_2$ -xylene-air mixtures.

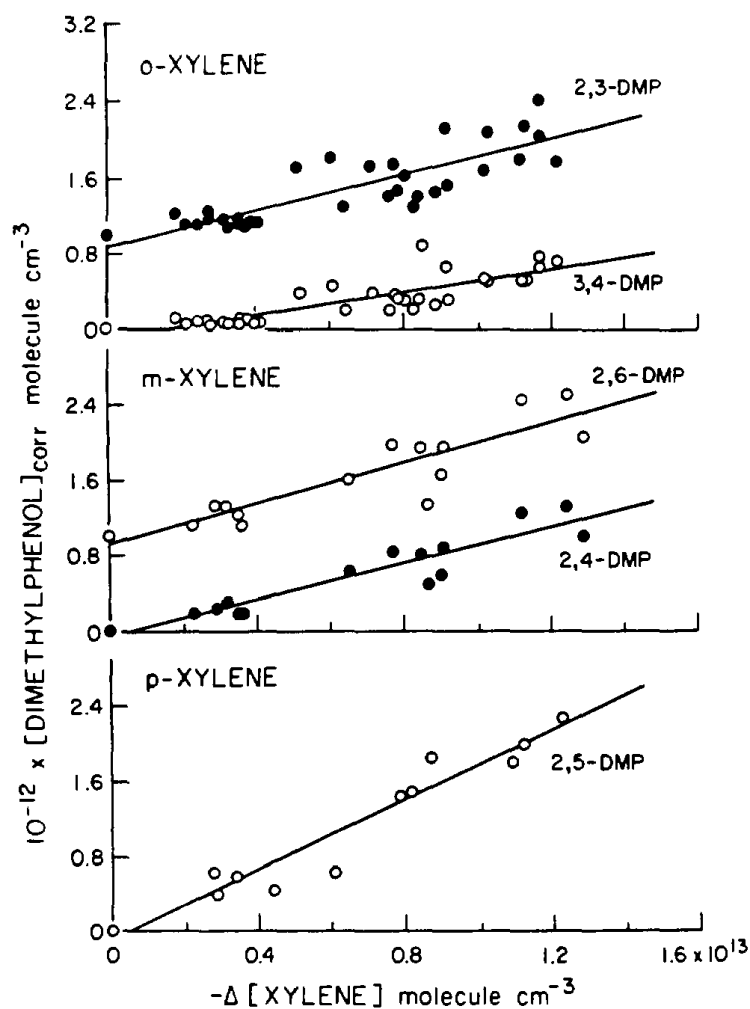


Figure V-8. Plots of the amounts of 2,3- and 3,4-dimethylphenol, 2,4- and 2,6-dimethylphenol, and 2,5-dimethylphenol (corrected to take into account reaction with the OH radical, see text) against the amounts of o-, m- and p-xylene, respectively, reacted in irradiated $\text{CH}_3\text{ONO-NO-NO}_2$ -xylene-air mixtures. (The data for 2,3- and 2,6-dimethylphenol have been displaced vertically by $1.0 \times 10^{12} \text{ molecule cm}^{-3}$ for clarity).

Table V-6. Comparison of the Present Results with Literature Data Concerning the Formation Yields of Aromatic Ring-Retaining Products Formed From the Gas-Phase Reactions of the OH Radical with Benzene, Toluene and the Xylenes Under Simulated Atmospheric Conditions

| Product | | Yield | Reference |
|---------|----------------|--|-------------------------|
| Benzene | Phenol | 0.236 ± 0.044 | This work |
| | Nitrobenzene | $\{(0.0336 \pm 0.0078) + (3.07 \pm 0.92) \times 10^{-16} [\text{NO}_2]\}^{\text{a,b}}$ | This work |
| Toluene | Benzaldehyde | ~0.5 | Spicer and Jones (1977) |
| | | 0.025 | O'Brien et al. (1979a) |
| | | 0.12 | Atkinson et al. (1980) |
| | | 0.073 ± 0.022 | Atkinson et al. (1983) |
| | | 0.054 | Shepson et al. (1984) |
| | | 0.071 | Leone et al. (1985) |
| | | 0.11 ± 0.01 | Bandow et al. (1985) |
| | | 0.104 ± 0.029 | Gery et al. (1985) |
| | Benzyl nitrate | $0.0645 \pm 0.0080^{\text{b}}$ | This work |
| | | 0.007 ± 0.004 | Gery et al. (1985) |
| | o-Cresol | $0.0084 \pm 0.0017^{\text{b}}$ | This work |
| | | ~0.15 | Spicer and Jones (1977) |
| | | 0.05 | O'Brien et al. (1979a) |
| | | 0.21 | Atkinson et al. (1980) |
| | | 0.131 ± 0.072 | Atkinson et al. (1983) |

Table V-6 (continued) - 2

| Product | | Yield | Reference |
|----------|----------------|--|----------------------------|
| o-Xylene | o-Tolualdehyde | 0.16 | Leone et al. (1985) |
| | | 0.22 | Gery et al. (1985) |
| | | 0.204 ± 0.027^b | This work |
| | | 0.05 | Gery et al. (1985) |
| | | 0.048 ± 0.009^b | This work |
| o-Xylene | o-Tolualdehyde | 0.07 ^c | Gery et al. (1985) |
| | | $\{(0.0135 \pm 0.0029) +$ | This work |
| | | $(1.90 \pm 0.25) \times 10^{-16} [\text{NO}_2]\}^{\text{a,b}}$ | |
| | | 0.073 \pm 0.036 | Takagi et al. (1980) |
| | | 0.047 | Shepson et al. (1984) |
| o-Xylene | o-Tolualdehyde | 0.05 \pm 0.01 | Bandow and Washida (1985a) |
| | | 0.172 \pm 0.070 | Gery et al. (1987) |
| | | 0.0453 ± 0.0059^b | This work |
| | | 0.009 \pm 0.002 | Takagi et al. (1980) |
| | | -0.012 | Gery et al. (1987) |
| o-Xylene | o-Tolualdehyde | $\{(0.0135 \pm 0.0051) +$ | This work |
| | | $(5.5 \pm 4.6) \times 10^{-17} [\text{NO}_2]\}^{\text{a,b}}$ | |
| | | 0.097 \pm 0.024 ^b | This work |
| | | | |
| | | | |

Table V-6 (continued) - 3

| Product | | Yield | Reference |
|----------|---------------------------|---|---|
| | 3,4-Dimethylphenol | 0.064 ± 0.015^b | This work |
| | 2,3- + 3,4-Dimethylphenol | 0.012 ± 0.006 0.102 ± 0.039^d | Takagi et al. (1980) Gery et al. (1987) |
| | 3-Nitro-o-xylene | 0.005 ± 0.002 $0.0059 \pm 0.0018^{b,e}$ | Takagi et al. (1980) This work |
| | 4-Nitro-o-xylene | 0.075 ± 0.045 $\{(0.0111 \pm 0.0029) +$ $(9.9 \pm 2.2) \times 10^{-17} [\text{NO}_2]\}^{a,b}$ | Takagi et al. (1980) This work |
| | Nitro-o-xylenes | 0.068 ± 0.019^f | Gery et al. (1987) |
| m-Xylene | m-Tolualdehyde | 0.04 ± 0.01 0.122 ± 0.059 0.0331 ± 0.0041^b | Bandow and Washida (1985a) Gery et al. (1987) This work |
| | 3-Methylbenzyl nitrate | ~ 0.010 $0.0061 \pm 0.0027^{b,e}$ | Gery et al. (1987) This work |
| | 2,4-Dimethylphenol | 0.099 ± 0.023^b | This work |

Table V-6 (continued) - 4

| Xylene | Product | Yield | Reference |
|----------|---------------------------|---|----------------------------|
| | 2,6-Dimethylphenol | 0.111 ± 0.033^b | This work |
| | 2,4- + 2,6-Dimethylphenol | 0.178 ± 0.065^g | Gery et al. (1987) |
| | 4-Nitro-m-xylene | $0.0018 \pm 0.0009^{b,e}$ | This work |
| | 5-Nitro-m-xylene | $\{(0.0032 \pm 0.0012) + (1.6 \pm 0.8) \times 10^{-17} [\text{NO}_2]\}^{a,b}$ | This work |
| | Nitro-m-xylenes | 0.033 ± 0.025^h | Gery et al. (1987) |
| p-Xylene | p-Tolualdehyde | 0.08 ± 0.01 | Bandow and Washida (1985a) |
| | | 0.10 | Becker and Klein (1987) |
| | | 0.0701 ± 0.0103^b | This work |
| | 4-Methylbenzyl nitrate | $0.0082 \pm 0.0016^{b,e}$ | This work |
| | 2,5-Dimethylphenol | 0.188 ± 0.038^b | This work |
| | 2-Nitro-p-xylene | $\{(0.0120 \pm 0.0035) + (2.8 \pm 2.6) \times 10^{-17} [\text{NO}_2]\}^{a,b}$ | This work |

Table V-6 (continued) - 5

^aNO₂ concentration in molecule cm⁻³ units.

^bIndicated error limits are the two least-squares standard deviations combined with an estimated GC-FID calibration uncertainty of ±10%.

^cAt a NO_x concentration of $\sim 2.4 \times 10^{14}$ molecule cm⁻³.

^d2,3-Dimethylphenol:3,4-dimethylphenol = $74 \pm 11:26 \pm 11$.

^eYield extrapolated to zero NO₂ concentration; dependence of yield on NO₂ concentration zero within two least-squares standard deviations.

^f4-Nitro-o-xylene accounted for $86 \pm 7\%$ of total; remainder 3-nitro-o-xylene.

^g2,4-Dimethylphenol:2,6-dimethylphenol = $58 \pm 19:42 \pm 19$; no 3,5-dimethylphenol observed.

^hMainly ($71 \pm 49\%$) 4-nitro-m-xylene; remainder 5-nitro-m-xylene.

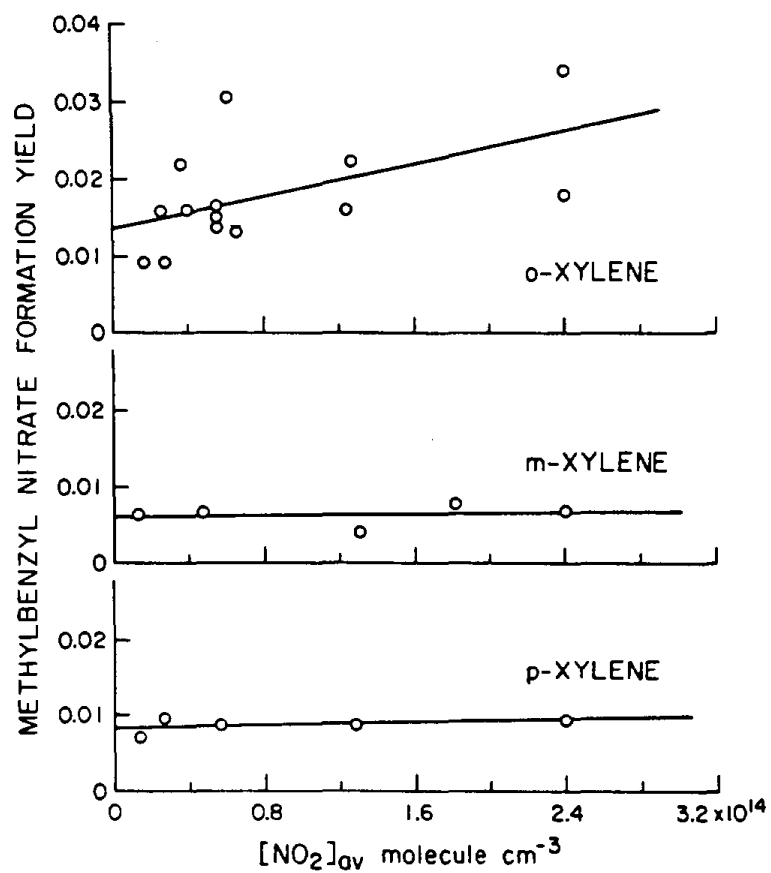


Figure V-9. Plots of the formation yields of 2-, 3- and 4-methylbenzyl nitrate from o-, m- and p-xylene, respectively, against the average NO_2 concentrations during the experiments.

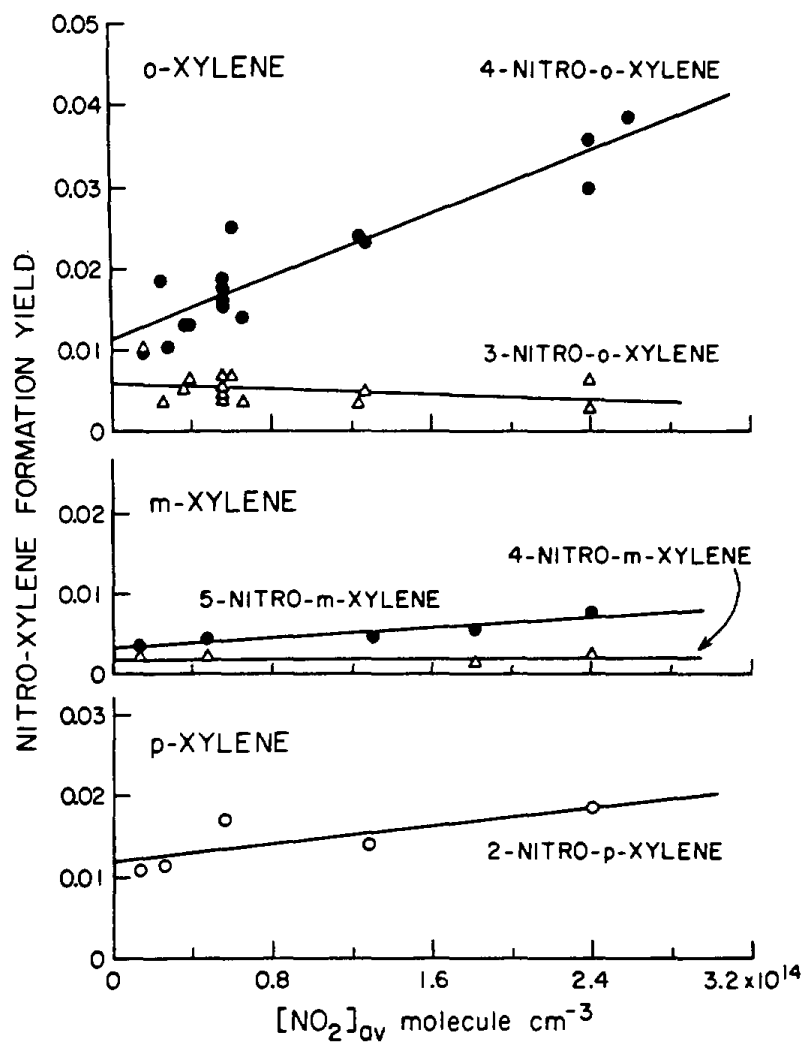


Figure V-10. Plots of the formation yields of the nitro-xylenes from o-, m- and p-xylene against the average NO_2 concentrations during the experiments.

experimental uncertainties. In addition, the 3-nitro-o-xylene formed did not always appear to increase linearly with the amount of o-xylene reacted (Table V-4), again leading to large uncertainties in the formation yields (the two least-squares standard deviations being of a similar magnitude to the formation yields in many cases).

As can be seen from the plots in Figures V-9 and V-10 and the least-squares formation yield data given in Table V-6, the formation yields of 3-nitro-o-xylene from o-xylene, 3-methylbenzyl nitrate and 4-nitro-m-xylene from m-xylene, and 4-methylbenzyl nitrate from p-xylene exhibited no dependence on the NO_2 concentration within the two least-squares standard deviations. Furthermore, any dependencies of the formation yields on the NO_2 concentration were close to the experimental uncertainties for 2-methylbenzyl nitrate from o-xylene and 2-nitro-p-xylene from p-xylene. Only for the formation of 4-nitro-o-xylene from o-xylene was there a clear dependence of the formation yield on the NO_2 concentration (Figure V-10 and Table V-6). For all of the methylbenzyl nitrates and the nitro-xylenes (noting the problems with the low amounts formed in certain cases and the above noted problems with the formation of 3-nitro-o-xylene from o-xylene), the formation yields extrapolated to zero NO_2 concentration were positive and were greater than four least-squares standard deviations from zero.

3. Discussion

The ring-retaining products observed in this work from the OH radical-initiated reactions of benzene, toluene and the xylenes (in the presence of NO_x) at room temperature and atmospheric pressure are compared with the available literature data in Table V-6.

Benzene. Phenol and nitrobenzene have previously been observed as products of the OH radical reaction with benzene by Hoshino et al. (1978) and Bandow et al. (1985). However, no formation yields have been reported prior to the present study.

Toluene. The ring-retaining products observed in this work have been previously reported from several studies. For benzaldehyde, the present formation yield is in reasonable agreement with those of Atkinson et al. (1980, 1983), Shepson et al. (1984), Leone et al. (1985), Bandow et al. (1985) and Gery et al. (1985). The benzaldehyde yields reported by Spicer and Jones (1977) and O'Brien et al. (1979a) are widely divergent and must

be judged to be incorrect. While benzyl nitrate was reported as a product in the previous studies of Hoshino et al. (1978), O'Brien et al. (1979b), Atkinson et al. (1980) and Gery et al. (1985), the only quantitative data concerning the benzyl nitrate yield arise from the studies of Hoshino et al. (1978) and Gery et al. (1985). Hoshino et al. (1978) determined a formation yield ratio of benzyl nitrate/benzaldehyde of 0.12, in excellent agreement with the present ratio of 0.13. The benzyl nitrate yield determined here is in good agreement with that of 0.007 ± 0.004 reported by Gery et al. (1985).

The formation of the cresol isomers have been reported previously (Table V-6), although, as in this work, m- and p-cresol were generally not separated by the analytical techniques used. For o-cresol, the present formation yield of 0.204 ± 0.027 agrees well with the values of Atkinson et al. (1980), Leone et al. (1985) and Gery et al. (1985), but is significantly higher than the formation yield derived by O'Brien et al. (1979a). Furthermore, the present data for m- and p-cresol are in excellent agreement with the value of Gery et al. (1985). Previous studies obtained formation yield ratios of o-cresol: m- + p-cresol of 80:20 (Hoshino et al., 1978) and o-cresol: m-cresol: p-cresol of 81:2:17 (Gery et al., 1985), in excellent agreement with our ratio of o-cresol: m- + p-cresol of 81:19.

Nitrotoluenes have been identified as products of the OH radical reaction with toluene under simulated atmospheric conditions in several previous studies. Hoshino et al. (1978) observed m- and p-nitrotoluene, but no o-nitrotoluene, with the p-nitrotoluene yield generally being less than that of the m-nitrotoluene isomer. O'Brien et al. (1979b) also observed only m- and p-nitrotoluene (although o-nitrotoluene and benzyl nitrate co-eluted, the peak was shown to be due to benzyl nitrate and not to o-nitrotoluene). Gery et al. (1985) observed the formation of all three nitrotoluene isomers, with the formation yield ratio o-nitrotoluene: m-nitrotoluene: p-nitrotoluene being 7:72:21, in good agreement with the present GC-MS ratio of 5:70:25. The data presented by Gery et al. (1985) allow an m-nitrotoluene formation yield of 0.07 to be calculated for an average inlet (to the stirred flow reactor) NO_x concentration of 2.4×10^{14} molecule cm^{-3} . While this value compares well with our formation yield of 0.06 at that concentration of NO_2 , the NO_2/NO_x concentration

ratio would be less than unity in the experiments of Gery et al. (1985), and hence the corresponding formation yield calculated from our data will be somewhere between 0.014 and 0.06.

o-Xylene. The ring-retaining products observed in this study agree with the previous observations of Takagi et al. (1980), Shepson et al. (1984), Bandow and Washida (1985a) and Gery et al. (1987) (Table V-6). The formation yield of o-tolualdehyde determined here is in excellent agreement with the data of Shepson et al. (1984) and Bandow and Washida (1985a) and is in reasonable agreement with the yield reported by Takagi et al. (1980), but is a factor of 3.8 lower than the yield measured by Gery et al. (1987). The present 2-methylbenzyl nitrate formation yield agrees well with the previous data (Takagi et al., 1980; Gery et al., 1987). While the overall dimethylphenol yield and the isomer distribution measured here are reasonably consistent with the data of Gery et al. (1987), the total dimethylphenol yield is an order of magnitude higher than that reported by Takagi et al. (1980). That the present dimethylphenol yield is higher than the previous measurements may be due to the high reactivity of the dimethylphenols, relative to o-xylene, and to neglect of (Takagi et al., 1980), or incomplete accounting for (Gery et al., 1987), the secondary reactions of the dimethylphenols in the reaction systems employed. The nitro-o-xylene yields reported by Takagi et al. (1980) and Gery et al. (1987) are reasonably consistent with the present data, with the 3-nitro-o-xylene yields measured by Takagi et al. (1980) and Gery et al. (1987) at initial NO_x concentrations of $(0.48-2.5) \times 10^{14}$ molecule cm^{-3} of 0.005 and 0.01, respectively, being in agreement with the present yield of 0.0059, independent of the NO_2 concentration. Furthermore, while a factor of ~3 higher than the present data, the 4-nitro-o-xylene yield determined by Takagi et al. (1980) increased with the initial NO_x concentration over the range $(0.48-2.5) \times 10^{14}$ molecule cm^{-3} , from 0.028 at 4.8×10^{13} molecule cm^{-3} to 0.062-0.136 at $(2.3-2.5) \times 10^{14}$ molecule cm^{-3} .

m-Xylene. The available ring-retaining product formation yields are given in Table V-6. Again, the ring-retaining products observed in this work are in agreement with previous studies (Bandow and Washida, 1985a; Gery et al., 1987), the most extensive of which was that of Gery et al. (1987). The present m-tolualdehyde formation yield is in good agreement

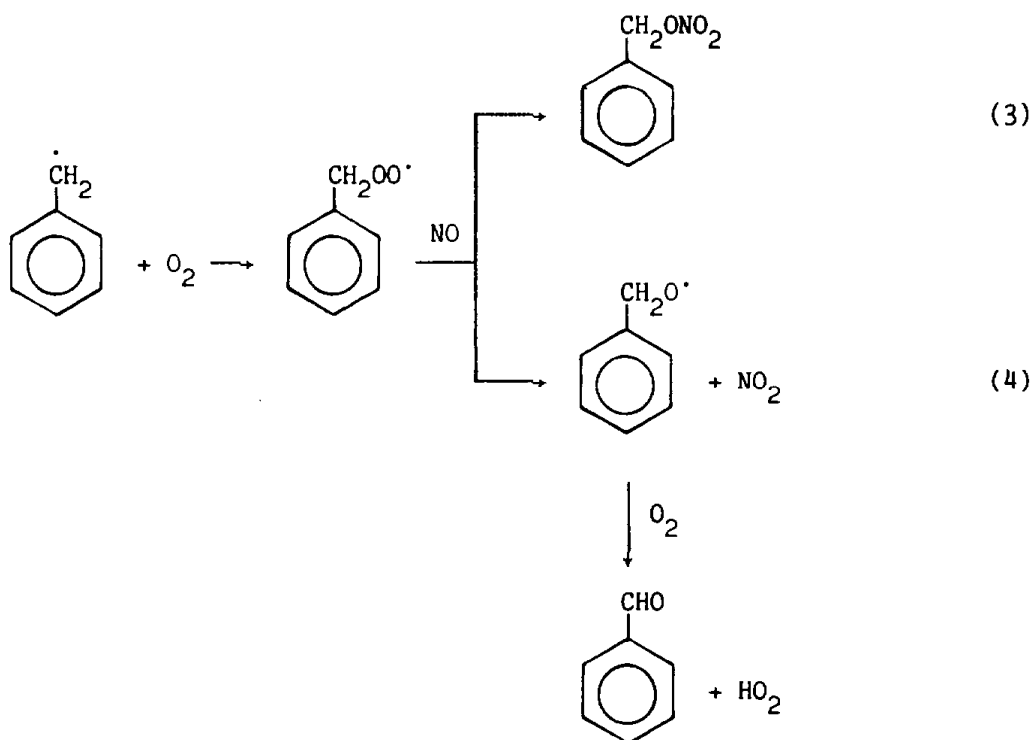
with that of Badow and Washida (1985a), but is a factor of 3.7 lower than the yield reported by Gery et al. (1987). However, the present 3-methylbenzyl nitrate yield agrees well with that of Gery et al. (1987). The overall dimethylphenol yield and the isomer distribution measured here are in agreement with the data of Gery et al. (1987) [it should be noted that the relative importance of secondary reactions of the dimethylphenols is less in the m-xylene system than in the o-xylene system]. In agreement with the observations of Gery et al. (1987), the major nitro-m-xylene formed is the 5-isomer, with the 2-nitro-m-xylene not being observed in either study. However, the nitro-m-xylene yields measured by Gery et al. (1987) at an initial NO_x concentration of $\sim 1.9 \times 10^{14}$ molecule cm^{-3} are significantly higher than the present data, by a factor of 2-4.

p-Xylene. The available ring-retaining product data are given in Table V-6. The only literature data concern the formation of p-tolualdehyde, and the yields determined by Becker and Klein (1987) and, especially, Badow and Washida (1985a) are in good agreement with our present data.

Mechanistic Implications. The present data for the formation of phenol from benzene, benzaldehyde, benzyl nitrate, and the cresols from toluene and the tolualdehydes, dimethylphenols, methylbenzyl nitrates and nitro-xylenes from the xylenes are in general agreement with the available literature data. However, the present study provides the first reported phenol yield from benzene and shows that while in some cases the nitro-aromatic formation yields increase approximately linearly with the NO_2 concentration, in all cases the formation yields of these products extrapolate to a non-zero value as the NO_2 concentration approaches zero.

As noted above, these OH radical reactions proceed by H-atom abstraction (from the substituent alkyl groups and from the C-H bonds of the aromatic ring) [reaction (1)] and by OH radical addition to the aromatic ring [reaction (2)]. Evaluation of the kinetic data (Atkinson, 1989) yields the rate constant ratio $k_1/(k_1 + k_2)$ (for toluene) = 0.12 at 298 K (with an estimated uncertainty of $\sim \pm 50\%$).

The reactions of the benzyl radical under atmospheric conditions are expected to be (Atkinson and Lloyd, 1984; Atkinson, 1990)



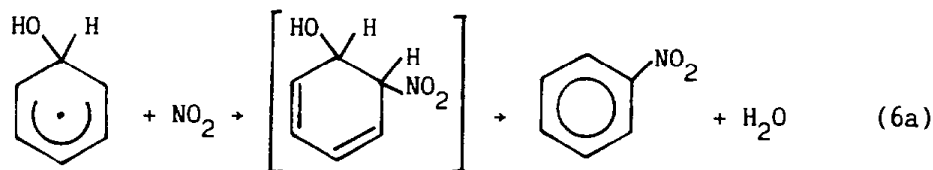
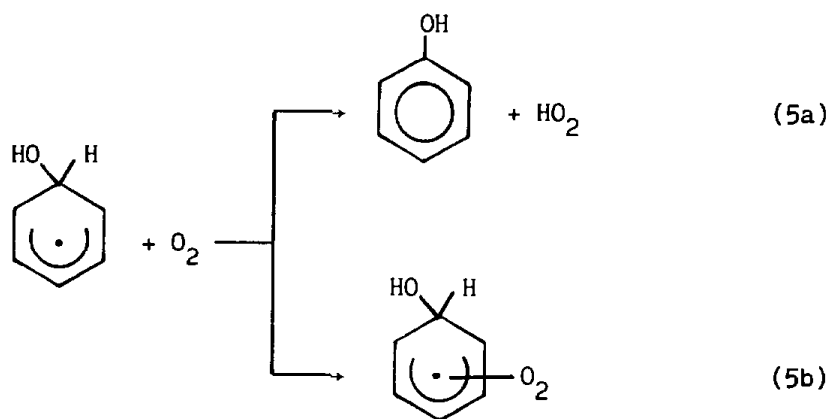
Thus, the sum of the formation yields of the aromatic-aldehyde and benzyl or methylbenzyl nitrate should equal the rate constant ratio $k_1/(k_1 + k_2)$. The sums of these product yields (0.073, 0.059, 0.039 and 0.078 for toluene, o-xylene, m-xylene and p-xylene, respectively) are reasonably consistent with the values of $k_1/(k_1 + k_2)$ derived from the kinetic data (Atkinson, 1989) of 0.12, 0.09, 0.05 and 0.09, respectively.

The reactions subsequent to the OH radical addition reaction (2) are not completely understood at the present time. In particular, the reactions under tropospheric conditions of the hydroxycyclohexadienyl and alkyl-substituted hydroxycyclohexadienyl radicals formed by OH radical addition to the aromatic ring, leading to ring-retaining and ring-cleavage products, are not known. Rate constants have been determined for the gas-phase reactions of the hydroxycyclohexadienyl and methylcyclohexadienyl radicals formed from benzene and toluene with NO (Zellner et al., 1985; Zetzsch et al., 1989), NO₂ (Zellner et al., 1985; Zetzsch et al., 1989) and O₂ (Zellner et al., 1985). The most recent and extensive data of Zetzsch et al. (1989) show that while these hydroxycyclohexadienyl radicals react rapidly with NO₂ (with rate constants of (2-4) x 10⁻¹¹ cm³

molecule⁻¹ s⁻¹ at room temperature), the reaction with NO is slow, with upper limits to the rate constants of $\leq (1-3) \times 10^{-14}$ cm³ molecule⁻¹ s⁻¹ (Zetzsch et al., 1989). Moreover, based upon the experimental data presented by Zellner et al. (1985), an upper limit to the rate constant for the reaction of the hydroxycyclohexadienyl radical with O₂ of $< 2 \times 10^{-16}$ cm³ molecule⁻¹ s⁻¹ can be estimated.

However, these kinetic studies, which did not detect any reaction of O₂ with the hydroxycyclohexadienyl radicals formed in reaction (2), do not preclude reaction with O₂ being dominant under atmospheric conditions (or indeed under the experimental conditions employed in this study, since the O₂/NO₂ concentration ratio was $\geq 10^4$).

The presently accepted chemical mechanisms assume that the hydroxycyclohexadienyl radicals formed in reaction (2) react with O₂ as well as with NO₂. For example, in the case of benzene the reactions have been assumed to be,

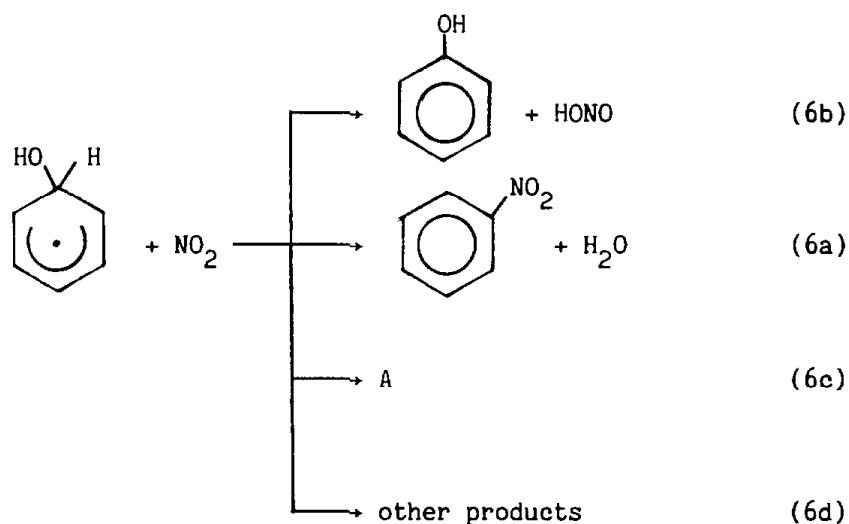


followed by subsequent reactions of the HO-aromatic-O₂ adduct formed in reaction (5b) leading to ring-opened products (Atkinson and Lloyd, 1984). With this reaction scheme, the nitroaromatic product yield(s) are predicted to be proportional to the NO₂/O₂ concentration ratio and thus extrapolate linearly to zero as the NO₂ concentration approaches zero.

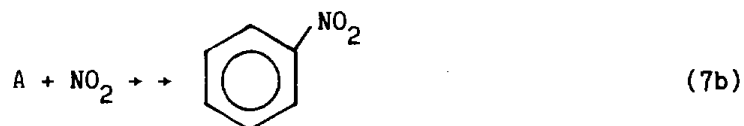
The present observations that the nitroaromatic formation yields do not approach zero as the NO₂ concentration approaches zero are clearly not consistent with the above mechanism. Rather, our data imply that the competing processes controlling the formation of the nitroaromatics and of other primary products at low NO_x concentrations either (a) do not involve NO_x, but instead involve the formation of some nitroaromatic precursor species which then reacts to form the nitroaromatic, or (b) involve only reactions with NO_x. In particular, the reactions controlling nitroaromatic formation cannot involve competition between a reaction with NO_x and some process(es) not involving NO_x (such as reaction with O₂), as assumed in the presently accepted mechanisms. Since the hydroxycyclohexadienyl radical reacts only slowly with O₂, if at all, it appears that the more likely possibility is alternative (b).

These data of Zetzsch et al. (1989), that reaction of the hydroxycyclohexadienyl radicals with NO₂ is much more rapid than reaction with NO, is consistent with the present data which do not show any obvious dependence of the nitroaromatic formation yields on the NO concentration or on the NO/NO₂ concentration ratio (compare, for example, runs ITC-1293 and 1298 for benzene and runs ITC-1263, 1267 and 1277 for toluene). However, the observation that the nitroaromatic formation yield increases as the NO₂ concentration increases indicates that there must be a second reaction pathway leading to nitroaromatic formation, with this second reaction route involving competition between an NO₂ reaction and another process. The observed lack of dependence of the nitroaromatic yields on the NO concentration indicates that this competitive reaction route also does not involve NO.

These observations suggest the following general reaction scheme for hydroxycyclohexadienyl radicals under our experimental conditions.



where A is an intermediate species which either reacts with NO_2 to form nitroaromatics or reacts with O_2 or unimolecularly to form other products

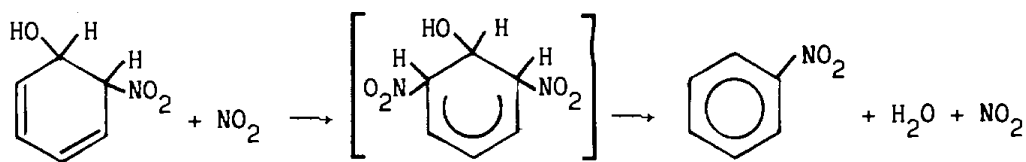


The "other products" formed in reactions (6d) and (7a) could include the various aromatic ring fragmentation products which are observed, but the available data are not sufficient to indicate the relative importance of these two possible routes.

This general reaction scheme is consistent with our experimental data in that it predicts that the nitroaromatic yields fit the equation

$$\text{nitroaromatic formation yield} = a + b [\text{NO}_2]$$

as observed (Figures V-4, V-6, V-9 and V-10). Although completely speculative, if the intermediate A is (for the benzene reaction) a hydroxy-nitro-1,3-cyclohexadiene, this species may add NO_2 and ultimately lead to the formation of nitroaromatics



Such a (speculative) reaction will be sterically hindered for alkyl and, especially, aryl substituent groups, and indeed the effect of NO₂ concentration on the nitroaromatic yield decreases along the series benzene > toluene > xylenes.

Under ambient atmospheric conditions, the m-nitrotoluene, nitrobenzene and nitroxylenes yields from toluene, benzene and the xylenes, respectively, are then expected to be similar to, or slightly greater than, the intercept values of the plots shown in Figures V-4, V-6, and V-10. Thus, these nitroaromatics, and by analogy the nitropolycyclic aromatic hydrocarbons (nitro-PAH), will be formed with non-negligible yields in the ambient atmosphere. While the NO₂ and NO concentrations employed in this study were generally higher than typical ambient urban atmospheric concentrations, the lower range of the NO and NO₂ concentrations employed here overlaps with those observed under ambient conditions. Therefore, assuming that the dependence of nitro-PAH yields on the NO₂ concentration is not greatly different from those observed here for nonfused aromatics, the nitro-PAH formation yields we have measured under laboratory conditions (~0.1% to 5%) (Arey et al., 1989 and references therein; Atkinson et al., 1990) should be reasonably applicable to ambient atmospheric conditions.

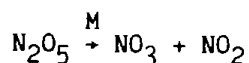
Thus, although the present work has resolved one previous inconsistency between laboratory data and ambient air measurements, it raises new and major problems concerning the mechanisms of the gas-phase reactions of the OH radical with aromatic hydrocarbons. While the observed NO to NO₂ conversion during the NO_x-air photooxidations of the aromatic hydrocarbons might be due, in large part, to the reactions of the products of these reactions, the pathways leading to ring cleavage need to be elucidated. Moreover, the dependence of the nitroaromatic yield on the NO₂ concentration observed in this study must be predicted by chemical mechanisms for the OH radical-initiated reactions of the aromatic hydrocarbons.

B. Hydroxynitro-Aromatic Formation from the OH and NO₃ Radical-Initiated Reactions of Phenol and o-Cresol

1. Experimental

Experiments were carried out in the 6400 liter all-Teflon chamber in a similar manner as described in Section V.A. above. To investigate the OH radical-initiated reactions, irradiations of CH₃ONO - NO - phenol - air and CH₃ONO - NO - o-cresol - air mixtures were carried out, with OH radicals being generated by the photolysis of methyl nitrite in air. The initial reactant concentrations in these experiments were (in units of 10¹³ molecule cm⁻³): CH₃ONO, 24; NO, 24; phenol, 3.8, or o-cresol, 2.4-2.5. Irradiations were carried out at 20% of the maximum light intensity for 2-20 mins (phenol) or 2-9 mins (o-cresol).

For the NO₃ radical-initiated reactions, NO₃ radicals were generated from the thermal decomposition of N₂O₅



and NO₂ was present to avoid secondary reactions and to extend the reactions beyond the mixing time. The initial reactant concentrations in these experiments were (in units of 10¹³ molecule cm⁻³): NO₂, 24; phenol, 3.3-3.4, or o-cresol, 2.4-3.1; and two additions of N₂O₅ [at initial concentrations in the chamber of (1.0-1.3) x 10¹³ molecule cm⁻³] were made to the chamber during the experiments.

Gas samples of 100 cm³ volume were withdrawn from the chamber onto Tenax GC solid adsorbent for analysis by GC-FID as described in Section V.A. above, using a 15 m Megabore DB-5 column. In addition, gas samples of 0.5-3 liter volume were collected on Tenax GC solid adsorbent for GC-MS analyses, as also described above.

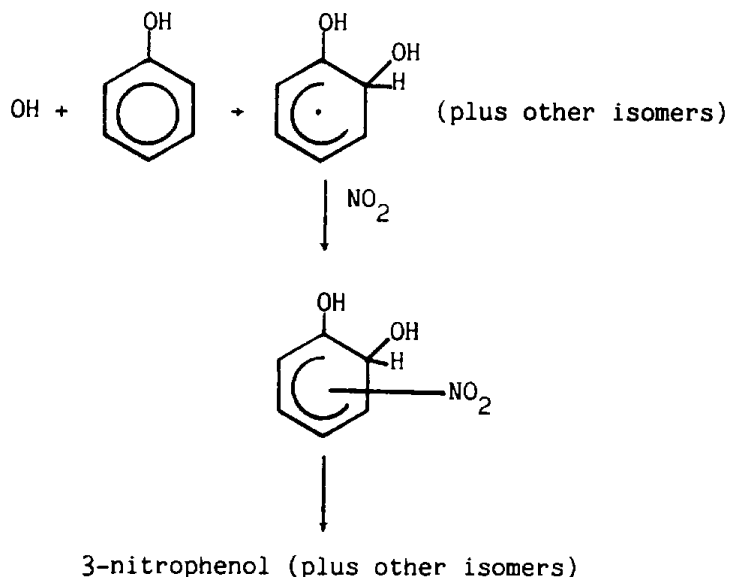
In addition to these experiments with phenol or o-cresol as the organic reactant, two CH₃ONO - NO - benzene - air (ITC-1579 and 1599) and one CH₃ONO - NO - toluene - air (ITC-1585) irradiations were carried out, these having initial CH₃ONO and NO concentrations, respectively, of (in units of 10¹³ molecule cm⁻³): 5.0 and 1.85 (ITC-1579); 2.5 and 0.99 (ITC-1585); and 27.1 and 0.95 (ITC-1599). These irradiations were carried out as described in Section V.A. above, with irradiation times of 2-20 min

(ITC-1579) and 2-14 min (ITC-1585), both at the maximum light intensity, and 2-10 min at 20% of the maximum light intensity (ITC-1599).

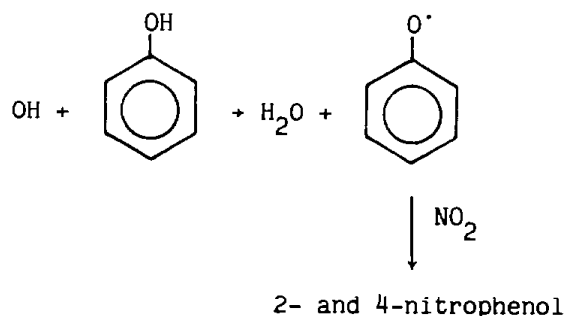
2. Results and Discussion

OH Radical Reactions with Phenol and o-Cresol. The products observed and quantified were 2-nitrophenol from phenol and 2-methyl-6-nitrophenol from o-cresol. Other product peaks observed in the GC-FID analyses and confirmed by the GC-MS analyses were 1,2-dihydroxybenzene (catechol) and 4-nitrophenol from phenol and 2-methyl-4-nitrophenol from o-cresol. Additionally, a dihydroxytoluene was tentatively identified from its mass spectrum as a product of the OH radical reactions with o-cresol.

Since 2-nitrophenol is ~30 times less reactive towards the OH radical than is phenol, reactive losses of the nitrophenols during the OH radical-initiated reactions of phenol and o-cresol were negligible, and hence no corrections for secondary reactions were necessary. Least-squares analyses of the experimental data yielded formation yields of 2-nitrophenol from phenol of 0.055 ± 0.015 and of 2-methyl-6-nitrophenol from o-cresol of 0.030 ± 0.014 , where the indicated errors are the two least-squares standard deviations combined with estimated overall uncertainties in the GC-FID calibration factors for the products and reactants of $\pm 10\%$ each. Two possible reaction routes leading to nitrophenol formation involve initial OH radical addition to the aromatic ring



and H-atom abstraction from the -OH group



The observation of 2-nitrophenol and 4-nitrophenol as products from phenol and of 2-methyl-6-nitrophenol and 2-methyl-4-nitrophenol from o-cresol are consistent with the reaction route involving H atom abstraction from the -OH substituent group. Furthermore, the measured formation yields of 2-nitrophenol and 2-methyl-6-nitrophenol are of a similar magnitude to the fractions of the overall OH radical reactions with phenol and o-cresol which proceed by H atom abstraction from the -OH group, of ~0.09 and ~0.06, respectively (Atkinson, 1989).

NO₃ Radical Reactions with Phenol and o-Cresol. Again, the products observed and quantified from the NO₃ radical-initiated reactions of phenol and o-cresol were 2-nitrophenol and 2-methyl-6-nitrophenol, respectively. In addition, 4-nitrophenol from phenol and 2-methyl-4-nitrophenol from cresol were identified as products in the GC-MS analyses of the NO₃ radical-initiated reactions. In the interpretation of the product data obtained, a major uncertainty concerns the rate constants for the reactions of the NO₃ radical with the nitrophenols and nitrocresols, relative to the rate constants for the parent phenol or cresol. Since the cresol rate constants are a factor of ~5 higher than that for phenol (Atkinson et al., 1988), it is expected that the nitrophenol products will be significantly less reactive towards the NO₃ radical than are the parent phenols. Hence, secondary reactions of the product nitrophenols with the NO₃ radicals during these reactions should be of minor significance. That this is the case is supported by the 2-methyl-6-nitrophenol product data from the NO₃ radical reactions with o-cresol. For an essentially identical amount of o-cresol reacted the measured amounts of 2-methyl-6-nitrophenol were in excellent agreement (Figure V-11), although the percentage

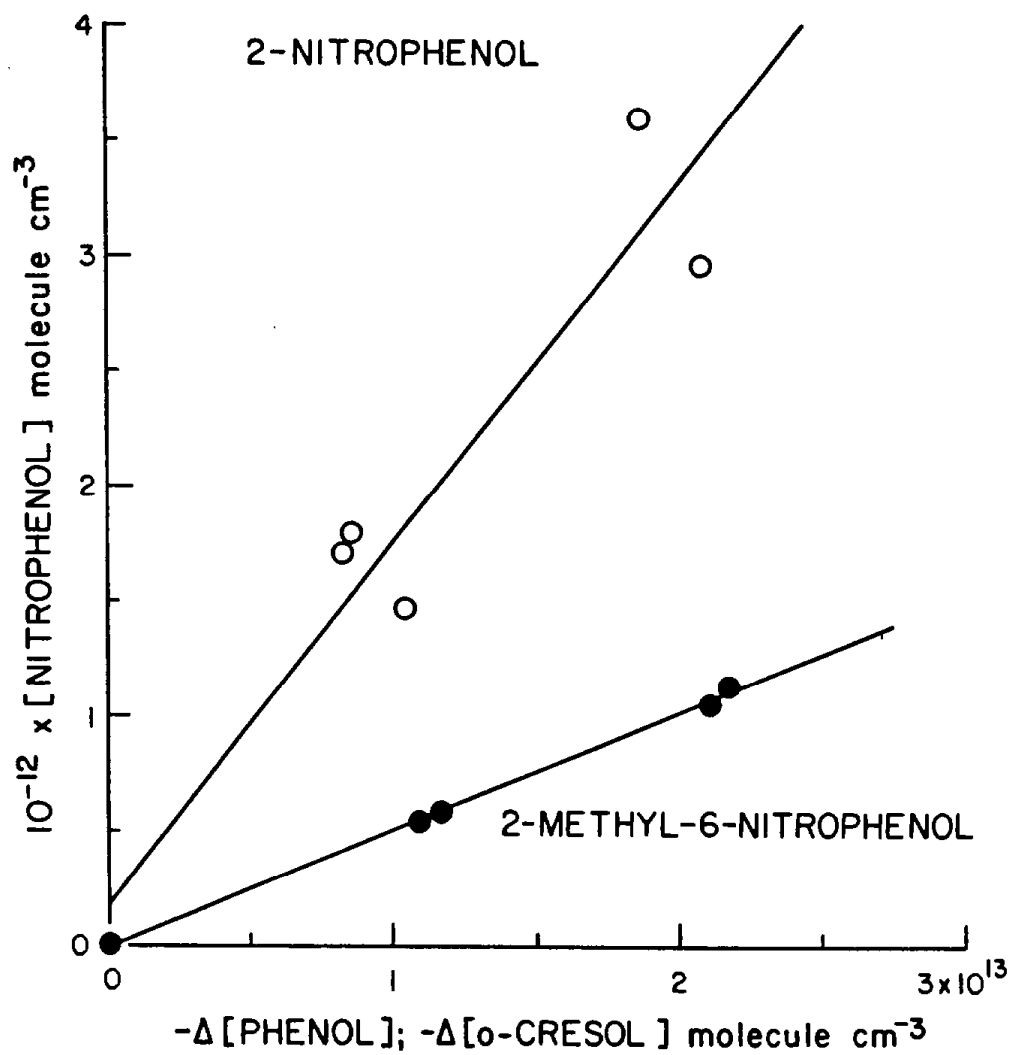
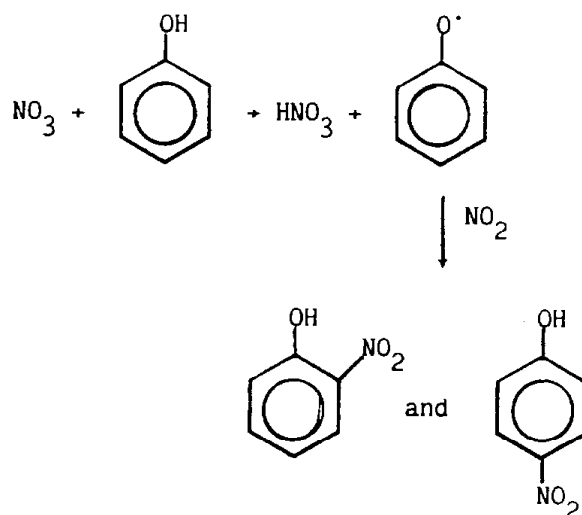


Figure V-11. Plots of the amounts of 2-nitrophenol and 2-methyl-6-nitrophenol against the amounts of phenol and o-cresol, respectively, reacted in $\text{N}_2\text{O}_5\text{-NO}_3\text{-NO}_2$ -air mixtures.

consumption of o-cresol in the two experiments were very different at 67% and 90%. If the nitrocresol reacted with the NO_3 radical with the same rate constant as o-cresol, the correction factors for these two experiments to take into account secondary reactions of the nitrocresol would differ by a factor of 2 and similar amounts of 2-methyl-6-nitrophenol formed from the same amount of o-cresol reacted would not be observed.

The amounts of the nitrophenols formed in these NO_3 radical reactions are plotted against the amounts of the parent phenols consumed in Figure V-11, assuming that the nitrophenol products are much less reactive towards the NO_3 radical than are the phenols. Good straight line plots are obtained, and least-squares analyses lead to product formation yields of 2-nitrophenol from phenol of 0.156 ± 0.057 and 2-methyl-6-nitrophenol from o-cresol of 0.051 ± 0.008 , where the indicated errors are the two least-squares standard deviations combined with estimated overall uncertainties of $\pm 10\%$ in the GC-FID calibration factors of the phenols and the nitrophenols. The present data are in general agreement with the previous observations of Grosjean (1985) of the formation of 2-methyl-6-nitrophenol and 2-methyl-4-nitrophenol from the reaction of the NO_3 radical with o-cresol, with a combined formation yield of 0.025-0.20. Taking into account the products formed and the rate constants for the reactions of the NO_3 radical with phenol and the cresols (see, for example, Atkinson et al., 1984, 1987), the reaction mechanism leading to the formation of the nitrophenols appears to be



and this reaction sequence is in agreement with the product study of Niki et al. (1979) of the Cl atom-initiated reaction of benzaldehyde in the presence of NO_x .

To determine whether or not the formation yields of 2-nitrophenol from phenol and of 2-methyl-6-nitrophenol from o-cresol are consistent with the nitrophenolic products formed from the OH radical-initiated reactions of benzene and toluene in the presence of NO_x , irradiations of $\text{CH}_3\text{ONO} - \text{NO} - \text{benzene} - \text{air}$ and $\text{CH}_3\text{ONO} - \text{NO} - \text{toluene} - \text{air}$ mixtures were carried out, with the goal being to generate sufficient NO_3 radicals during the latter stages of the irradiations, from the reaction,



that NO_3 radical reactions with the initially formed phenols became an important loss process. In accordance with the discussion in Section V.A. above, NO_3 radical reactions only became important under conditions where the NO_2/NO concentration ratio was $>7-8$, with OH radical reactions dominating when the NO_2/NO concentration ratio was $<7-8$.

The measured amounts of phenol and 2-nitrophenol are plotted against the amount of benzene reacted in Figure V-12. For run ITC-1579 (lower plot in Figure V-12) the NO_2/NO concentration ratio was always <5 , and only the OH radical reactions were operable in this irradiation. The solid lines in Figure V-12 (lower plot) show the predicted phenol and 2-nitrophenol concentrations, using the product yields determined in this work for the OH radical-initiated formation of phenol from benzene (taking into account OH radical reaction of the phenol) and of 2-nitrophenol from phenol. For run ITC-1579, the agreement between the measured and predicted concentrations is good.

During run ITC-1599 (Figure V-12, upper plot), the NO to NO_2 conversion was sufficient that reaction with the NO_3 radical was expected to become important, and the OH radical and NO_3 radical-dominated portions of this irradiation are shown by the solid and dashed lines, respectively. Again, the phenol concentration is calculated for its formation from benzene and subsequent loss, both by OH radical reaction. As expected, the measured phenol concentrations are in reasonable agreement with the predicted values when reaction of phenol was dominated by OH radical

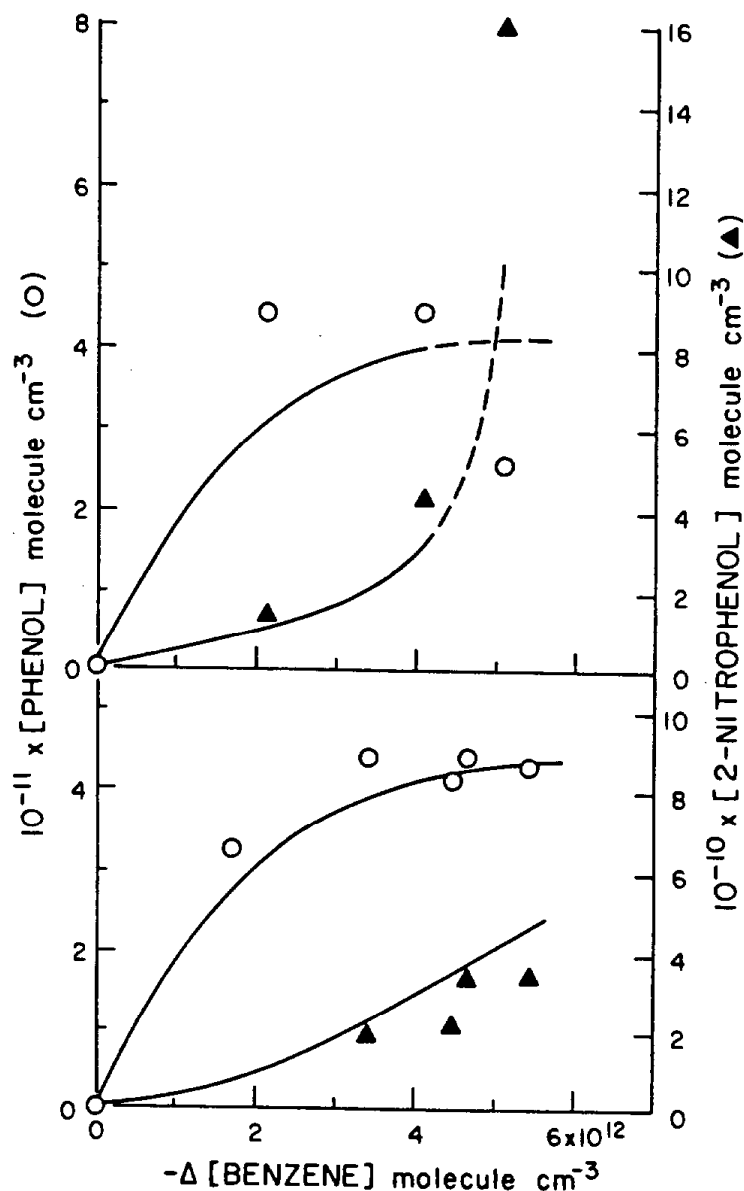


Figure V-12. Plots of the amounts of phenol (○) and 2-nitrophenol (▲) formed against the amounts of benzene consumed in irradiated $\text{CH}_3\text{ONO-NO-benzene-air}$ mixtures. The lines are the calculated phenol and 2-nitrophenol concentrations. The phenol data were calculated on the basis of only OH radical reaction and are shown as a dashed line (---) when NO_3 radical reaction would dominate as a phenol loss process. The calculated 2-nitrophenol concentrations from OH radical reaction of phenol are shown as the solid lines and the 2-nitrophenol concentration calculated for NO_3 radical reaction of phenol is shown as the dashed line. Upper plot, run ITC-1599; lower plot, run ITC-1579.

reaction, with a rapid decrease in the measured phenol concentration relative to the calculated curve occurring when the NO_3 radical reaction became important. The 2-nitrophenol concentration is initially calculated for its OH radical-initiated formation from phenol and then with the additional NO_3 radical-initiated formation (---) from phenol. The measured 2-nitrophenol concentration is in general agreement with the predictions, showing a sharp rise as the phenol concentration drops although the predicted 2-nitrophenol concentration did not increase as rapidly as measured values.

The toluene, o-cresol and 2-methyl-6-nitrophenol data are shown in Figure V-13 for the run ITC-1585, where again the solid and dashed lines denote the portions of the reaction when OH radical and NO_3 radical reaction, respectively, dominated as a loss process for the o-cresol. The agreement between the predicted and measured o-cresol concentrations is initially good during the OH radical reaction dominated portion of the run. Again, as expected, there is a marked decrease in the o-cresol concentration when the NO_3 radical reaction became important, and the measured and predicted 2-methyl-6-nitrophenol concentrations are in good agreement throughout the irradiation.

3. Conclusions

The product data obtained in this study provide important new information concerning the overall mechanisms of the OH radical-initiated reactions of the aromatic hydrocarbons. In particular, these data show that the nitroaromatic formation yields do not extrapolate to zero at low NO_2 concentrations, and it is hence expected that the nitroaromatic (and nitro-polycyclic aromatic hydrocarbons) products of these reactions will be formed under tropospheric conditions, in agreement with the presence of a number of nitro-PAH in ambient air that can only be formed in the atmosphere from the gas-phase reactions of the PAH (see Arey et al., 1989 and references therein). We conclude that the initially formed hydroxycyclohexadienyl-type radicals react with NO_2 and not with O_2 , at least for NO_2 concentrations $> 2 \times 10^{13}$ molecule cm^{-3} , and this finding necessitates the development of new chemical mechanisms for the atmospheric chemistry of the aromatic hydrocarbons.

While nitrophenols are formed from both the OH and NO_3 radical-initiated reactions of the phenols and cresols, the formation yields are

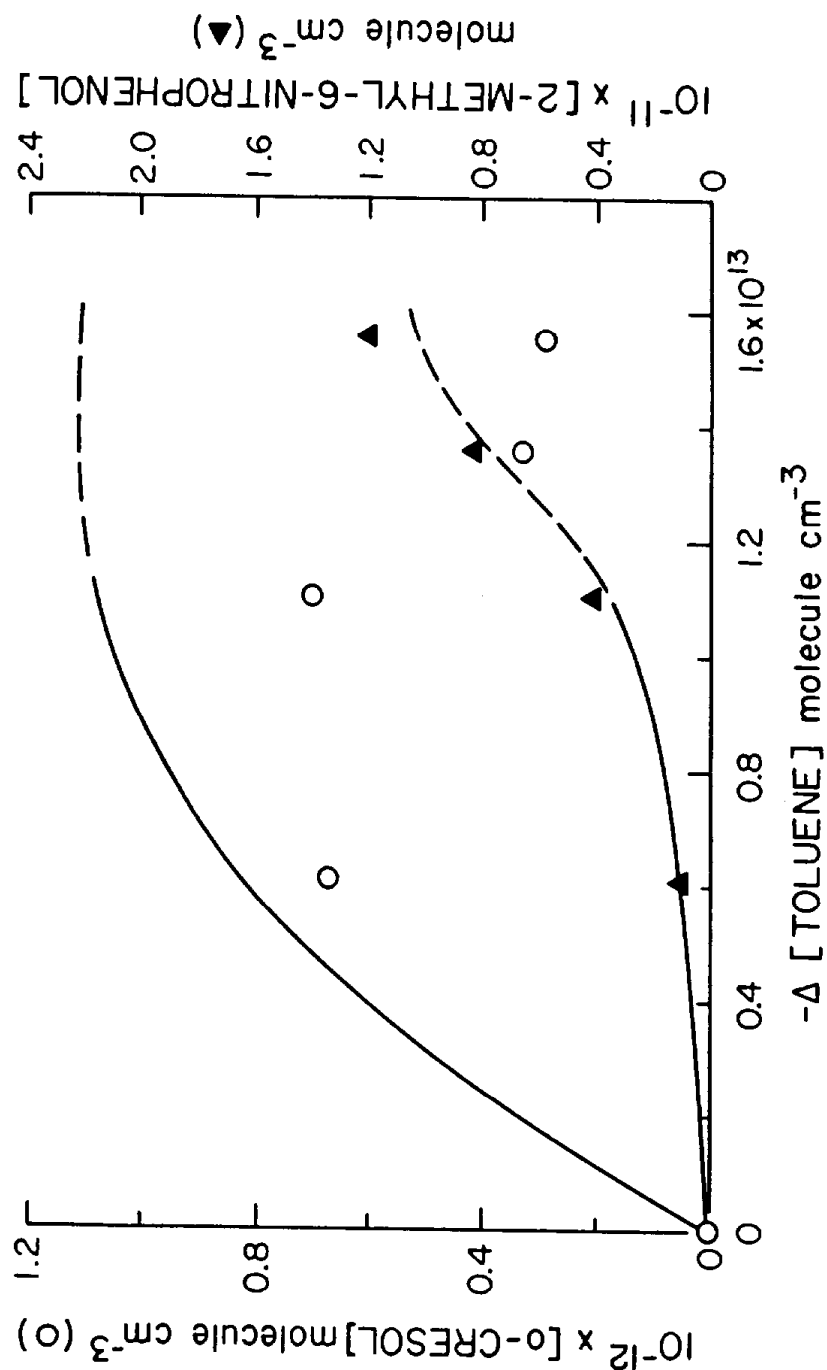


Figure V-13. Plots of the amounts of o-cresol (O) and 2-methyl-6-nitrocresol (▲) formed against the amount of toluene reacted in an irradiated $\text{CH}_3\text{ONO-NO}$ -toluene-air mixture (run ITC-1585). The lines are those calculated from the product yields and formation and loss reactions: (—) o-cresol reaction dominated by OH radical reaction; (---) o-cresol reaction dominated by NO_3 radical reaction, with the o-cresol data being calculated on the basis of only OH radical reaction.

fairly low, and large concentrations of nitrophenolic compounds relative to the parent aromatic species are not expected to be formed under atmospheric conditions. For example, the maximum yield of 2-nitrophenol from benzene (under conditions where the initially formed phenol is removed by reaction with the NO_3 radical) is ~3.5-4% of the benzene reacted, and the analogous maximum yield of 2-methyl-6-nitrophenol from toluene is ~1%. As always, the toxicological and ecological impacts of the products must be assessed before the importance of these atmospheric formation pathways can be evaluated.

VI. REFERENCES

- Arey, J., B. Zielinska, R. Atkinson and S. M. Aschmann (1989) *Int. J. Chem. Kinet.*, 21, 775.
- Atkinson, R., W. P. L. Carter, K. R. Darnall, A. M. Winer and J. N. Pitts, Jr. (1980) *Int. J. Chem. Kinet.*, 12, 779.
- Atkinson, R., S. M. Aschmann, D. R. Fitz, A. M. Winer and J. N. Pitts, Jr. (1982a) *Int. J. Chem. Kinet.*, 14, 13.
- Atkinson, R., S. M. Aschmann, W. P. L. Carter, A. M. Winer and J. N. Pitts, Jr. (1982b) *J. Phys. Chem.*, 86, 4563.
- Atkinson, R., W. P. L. Carter and A. M. Winer (1983) *J. Phys. Chem.*, 87, 1605.
- Atkinson, R. and W. P. L. Carter (1984) *Chem. Rev.*, 84, 437.
- Atkinson, R. and A. C. Lloyd (1984) *J. Phys. Chem. Ref. Data*, 13, 315.
- Atkinson, R., W. P. L. Carter, C. N. Plum, A. M. Winer and J. N. Pitts, Jr. (1984) *Int. J. Chem. Kinet.*, 16, 887.
- Atkinson, R., S. M. Aschmann, A. M. Winer and J. N. Pitts, Jr. (1985) *Arch. Environ. Contam. Toxicol.*, 14, 417.
- Atkinson, R., S. M. Aschmann and A. M. Winer (1987) *Environ. Sci. Technol.*, 21, 1123.
- Atkinson, R. (1988) pp. 99-132 in Air Pollution, the Automobile and Public Health, A. Y. Watson, R. R. Bates and D. Kennedy, Eds., National Academy Press, Washington, DC.
- Atkinson, R., S. M. Aschmann and J. N. Pitts, Jr. (1988) *J. Phys. Chem.*, 92, 3454.
- Atkinson, R. (1989) *J. Phys. Chem. Ref. Data*, Monograph 1, 1.
- Atkinson, R. (1990) *Atmos. Environ.*, 24A, 1.
- Atkinson, R., J. Arey, B. Zielinska and S. M. Aschmann (1990) *Int. J. Chem. Kinet.*, in press.
- Bandow, H. and N. Washida (1985a) *Bull. Chem. Soc. Jpn.*, 58, 2541.
- Bandow, H. and N. Washida (1985b) *Bull. Chem. Soc. Jpn.*, 58, 2549.
- Bandow, H., N. Washida and H. Akimoto (1985) *Bull. Chem. Soc. Jpn.*, 58, 2531.

- Becker, K. H. and Th Klein (1987) Proceedings, 4th European Symposium on the Physico-Chemical Behaviour of Atmospheric Pollutants, Riedel Publ. Co., Dordrecht, pp. 320-326.
- Bignozzi, C. A., A. Maldotti, C. Chiorboli, C. Bartocci and V. Carassiti (1981) Int. J. Chem. Kinet., 13, 1235.
- Bufalini, J. J. and A. P. Altshuller (1965) Can. J. Chem., 43, 2243.
- Carter, W. P. L. (1990) Atmos. Environ., 24A, 481.
- Darnall, K. R., R. Atkinson and J. N. Pitts, Jr. (1979) J. Phys. Chem., 83, 1943.
- Dumdei, B. E. and R. J. O'Brien (1984) Nature, 311, 248.
- Ferris, A. F., K. W. McLean, I. G. Marks and W. D. Emmons (1953) J. Am. Chem. Soc., 75, 4078.
- Gery, M. W., D. L. Fox, H. E. Jeffries, L. Stockburger and W. S. Weathers (1985) Int. J. Chem. Kinet., 17, 931.
- Gery, M. W., D. L. Fox, R. M. Kamens and L. Stockburger (1987) Environ. Sci. Technol., 21, 339.
- Grosjean, D. and K. Fung (1984) J. Air Pollut. Control Assoc., 34, 537.
- Grosjean, D. (1985) Environ. Sci. Technol., 19, 968.
- Hoshino, M., H. Akimoto and M. Okuda (1978) Bull. Chem. Soc. Jpn., 51, 718.
- Leone, J. A., R. C. Flagan, D. Grosjean and J. H. Seinfeld (1985) Int. J. Chem. Kinet., 17, 177.
- Lonneman, W. A., R. L. Seila and S. A. Meeks (1986) Environ. Sci. Technol., 20, 790.
- Nelson, P. F. and S. M. Quigley (1984) Atmos. Environ., 18, 79.
- Niki, H., P. D. Maker, C. M. Savage and L. P. Breitenbach (1979) pp. 1-16 in Nitrogenous Air Pollutants, D. Grosjean, Ed., Ann Arbor Press, Ann Arbor, MI.
- O'Brien, R. J., P. J. Green and R. M. Doty (1979a) pp. 93-95 in Chemical Kinetic Data Needs for Modeling the Lower Troposphere, NBS Special Publication 557, August.
- O'Brien, R. J., P. J. Green, R. A. Doty, J. W. Vanderzanden, R. R. Easton and R. P. Irwin (1979b) pp. 189-210 in Nitrogenous Air Pollutants, D. Grosjean, Ed., Ann Arbor Press, Ann Arbor, MI.
- Shepson, P. B., E. O. Edney and E. W. Corse (1984) J. Phys. Chem., 88, 4122.

- Sigsby, J. E., Jr., S. Tejada, W. Ray, J. M. Lang and J. W. Duncan (1987) Environ. Sci. Technol., 21, 466.
- Spicer, C. W. and P. W. Jones (1977) J. Air Pollut. Control Assoc., 27, 1122.
- Takagi, H., N. Washida, H. Akimoto, K. Nagasawa, Y. Usui and M. Okuda (1980) J. Phys. Chem., 84, 478.
- Takagi, H., N. Washida, H. Akimoto and M. Okuda (1982) Spectroscopy Lett., 15, 145.
- Taylor, W. D., T. D. Allston, M. J. Moscato, G. B. Fazekas, R. Kozlowski and G. A. Takacs (1980) Int. J. Chem. Kinet., 12, 231.
- Tuazon, E. C., R. Atkinson, H. Mac Leod, H. W. Biermann, A. M. Winer, W. P. L. Carter and J. N. Pitts, Jr. (1984) Environ. Sci. Technol., 18, 981.
- Tuazon, E. C., H. Mac Leod, R. Atkinson and W. P. L. Carter (1986) Environ. Sci. Technol., 20, 383.
- Zellner, R., B. Fritz and M. Preidel (1985) Chem. Phys. Lett., 121, 412.
- Zetzsch, C., R. Koch, M. Siese and F. Witte (1989) Proceedings, 5th European Symposium on the Physico-Chemical Behaviour of Atmospheric Pollutants, Riedel Publ. Co., Dordrecht, in press.
- Zweidinger, R. B., J. E. Sigsby, Jr., S. B. Tejada, F. D. Stump, D. L. Dropkin and W. D. Ray (1988) Environ. Sci. Technol., 22, 956.

APPENDIX A

ATMOSPHERIC LIFETIME AND FATE OF CHLOROFORM

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

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

Roger Atkinson and Arthur M. Winer

October 25, 1988

Statewide Air Pollution Research Center
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Riverside, CA 92521

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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 includes:

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

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

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

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

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

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

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

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

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

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

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

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

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

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

In this report, we describe the available literature data concerning the chemical and physical removal processes for chloroform, and estimate its resulting atmospheric lifetime. We will also briefly summarize some of the available literature concerning typical ambient atmospheric concentrations of chloroform. Chloroform is gaseous under atmospheric conditions, and hence only the gas-phase processes need be considered.

B. Chemical Loss Processes

1. Ozone

No experimental data are available concerning the rate constant for the gas-phase reaction of chloroform with ozone. However, the fact that any elementary reaction between O_3 and the alkanes has a room temperature rate constant of $\leq 10^{-23} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Atkinson and Carter 1984), combined with the lower reactivity of haloalkanes compared to the alkanes towards H-atom abstraction processes (Atkinson 1986, 1987), allows us to place an upper limit on the room temperature rate constant for the reaction of O_3 with CHCl_3 of $k(\text{O}_3 + \text{CHCl}_3) \leq 10^{-23} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

2. OH Radicals

Kinetic data for the reaction of OH radicals with chloroform have been obtained by Howard and Evenson (1976), Cox et al. (1976), Davis et al. (1976), Jeong and Kaufman (1982) and Klöpffer et al. (1986). These data are given in Table 1, and those of Howard and Evenson (1976), Cox et al. (1976), Davis et al. (1976) and Jeong and Kaufman (1982) are plotted in Arrhenius form in Figure 1 [both adapted from Atkinson (1989)].

The room temperature rate constant obtained from the relative rate study of Cox et al. (1976) is uncertain by a factor of ~ 2 , because of uncertainties in the number of NO to NO_2 conversions occurring after the initial OH radical reaction. The rate constant derived from the study of Klöpffer et al. (1986) is not used in the evaluation of the rate constant for this reaction because of a lack of details concerning their experimental conditions.

Table 1. Rate Constants k and Arrhenius Parameters ($k = A T^n e^{-B/T}$) for the Gas-Phase Reaction of the OH Radical with CHCl_3

| $10^{12} \times A$ ($\text{cm}^3 \text{mole}^{-1} \text{s}^{-1}$) | n | B (K) | $10^{14} \times k$ ($\text{cm}^3 \text{mole}^{-1} \text{s}^{-1}$) | at T (K) | Technique | Reference | Temperature range covered (K) |
|--|-----------------|--------------------------------|---|--|---|---|-------------------------------|
| | | | 10.1 ± 1.5 | 296 ± 2 | DF-LMR | Howard and Evenson (1976) | |
| | | | 20.0 | 298 | RR [relative to $k(\text{OH} + \text{methane}) = 8.36 \times 10^{-15} \text{a}$] | Cox et al. (1976) | |
| 4.69 ± 0.71 | | 1134 ± 108 | 4.39 ± 0.28 11.4 ± 0.7 21.8 ± 1.4 | 245 298 375 | FP-RF | Davis et al. (1976) | 245-375 |
| | | | 5.51 ± 0.41 | 249 | DF-RF | Jeong and Kaufman (1982), Jeong et al. (1984) | 249-487 |
| | | | 10.1 ± 0.65 16.0 ± 1.0 23.2 ± 1.6 30.8 ± 2.0 44.8 ± 2.7 55.0 ± 3.9 | 298 339 370 411 466 487 | | | |
| 6.91×10^{-8} 5.63 ± 0.68 | 2.65 ± 1.13 | 262 ± 398 1183 ± 45 | | | | RR [relative to $k(\text{OH} + \text{toluene}) = 5.91 \times 10^{-12} \text{a}$] | |
| | | | 29 | 300 | | Klopffer et al. (1986) | |

^aAs evaluated by Atkinson (1989).

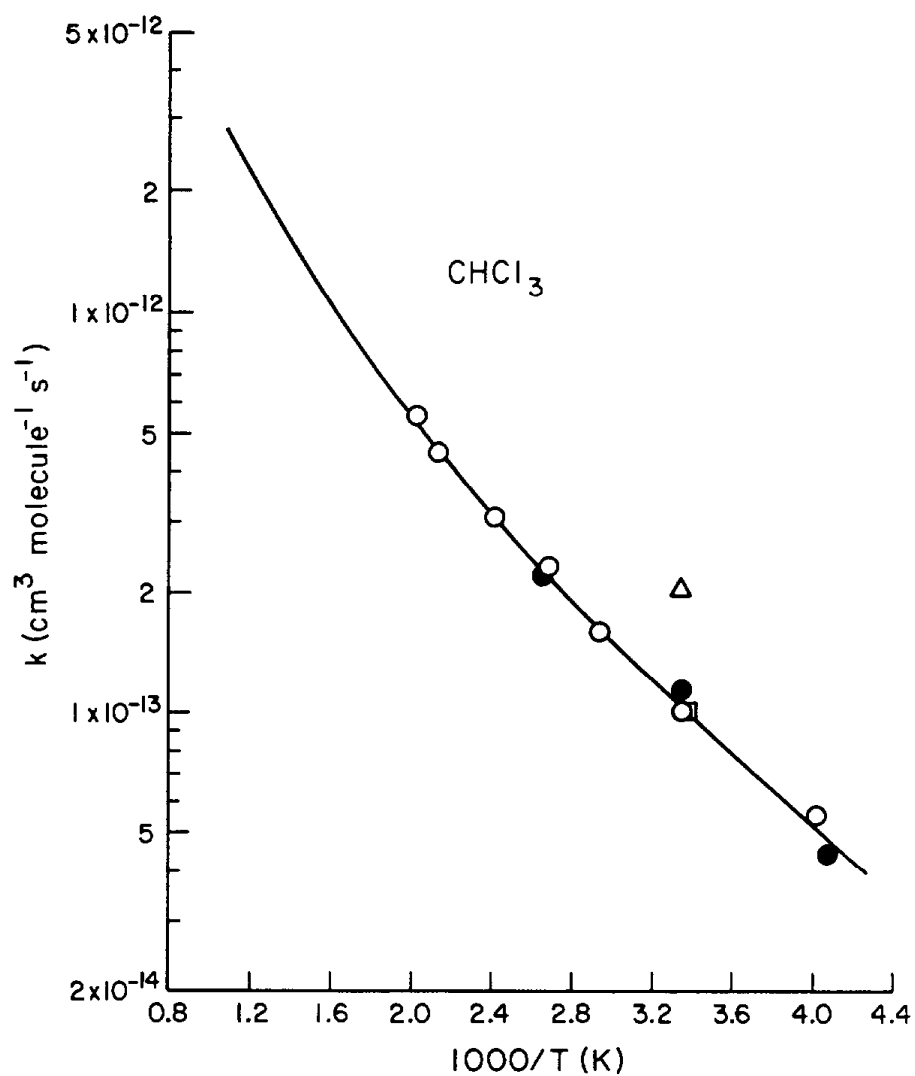


Figure 1. Available kinetic data for chloroform. Data from: ○ Jeong and Kaufman (1982), ● Davis et al. (1976), △ Cox et al. (1976), □ Howard and Evenson (1976).

It can be seen that the absolute rate constants of Howard and Evenson (1976), Davis et al. (1976) and Jeong and Kaufman (1982) are in excellent agreement. Thus, a unit-weighted, least-squares analysis of the data of Howard and Evenson (1976), Davis et al. (1976) and Jeong and Kaufman (1982), using the equation $k = AT^2e^{-B/T}$, yields the recommended expression of

$$k(\text{CHCl}_3) = (6.30^{+1.18}_{-1.00}) \times 10^{-18} T^2 e^{-(504 \pm 56)/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 245-487 K, where the error limits are two least-squares standard deviations (Atkinson 1989). From this expression, values of the rate constant for reaction of OH radicals with CHCl_3 at 298 K (room temperature) and 265 K (the average tropospheric temperature) are

$$k(\text{CHCl}_3) = 1.03 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K}$$

and

$$k(\text{CHCl}_3) = 6.6 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 265 \text{ K}$$

with an estimated overall uncertainty of $\pm 20\%$ at 298 K and $\pm 35\text{--}40\%$ at 265 K. The rate constant at 298 K is identical to those recommended by Atkinson (1986) and the recent NASA evaluation panel (DeMore et al. 1987).

3. NO_3 Radicals

No experimental data are available concerning the rate constant for gas-phase reaction of NO_3 radicals with chloroform. However, by analogy with the experimental data for the $\text{C}_4\text{--C}_9$ alkanes (Atkinson et al. 1988) and the observation that the rate constant for H-atom abstraction from CHCl_3 by OH radicals is lower than those for the $\geq \text{C}_2$ alkanes (Atkinson 1986, 1988), the room temperature rate constant for the reaction of NO_3 with CHCl_3 is expected to be $k(\text{NO}_3 + \text{CHCl}_3) < 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

4. Other Chemical Species

Based on chemical considerations, none of the other reactive species present in the troposphere (cited in the Introduction) are expected to react with chloroform, certainly not at rates which are significant relative to its rate of reaction with OH radicals.

5. Photolysis

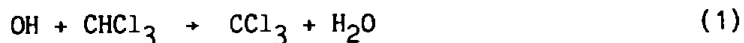
Several determinations of the absorption cross section of chloroform have been reported in the literature (Robbins 1977, Hubrich and Stuhl 1980, Simon et al. 1988). The long wavelength cutoff in the UV absorption spectrum of chloroform (the wavelength for which the absorption cross-section σ falls below a value which corresponds to photolysis being of negligible importance [i.e., $\sigma < 10^{-23} \text{ cm}^2$]) is reported to be at 260 nm (Hubrich and Stuhl, 1980). Based on these data, chloroform will not undergo photolysis in the troposphere at any measurable rate (WMO 1986, DeMore et al. 1987), since only radiation of wavelength $\geq 290 \text{ nm}$ penetrates into the troposphere.

Thus, the only significant chemical removal process for CHCl_3 in the troposphere is by reaction with the OH radical.

C. Atmospheric Reactions

Since the OH radical reaction is the only significant loss process, only this reaction need be considered in evaluating the products formed from the atmosphere degradation of CHCl_3 .

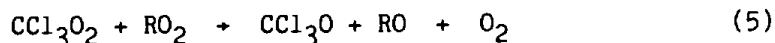
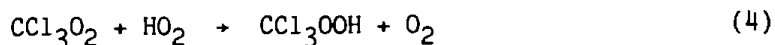
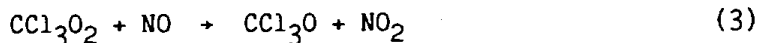
Chloroform is expected to undergo H-atom abstraction by OH radicals to form water and the CCl_3 radical



The CCl_3 radical will then react rapidly with molecular oxygen to form the peroxy radical (Cooper et al. 1980)



with a room temperature rate constant of $5.1 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, followed by reaction with NO (if present), HO_2 radicals or other peroxy radicals (RO_2) [Reactions (3-5)]



Only for the NO reaction is a rate constant available, of $1.7 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K (Dognon et al. 1985).

Although the reactions with HO_2 or RO_2 given above have not been experimentally studied, the products are those expected based upon other alkyl peroxy radical reactions.

The CCl_3O radical then undergoes rapid unimolecular decomposition to produce COCl_2 (phosgene) and a Cl atom (Rayez et al. 1987), with a rate constant $>1 \times 10^5 \text{ sec}^{-1}$ at 298 K. The Cl atoms will react with other organics (mainly CH_4) present in the atmosphere to yield HCl which is then rained out of the troposphere.

D. Physical Loss Processes

Information concerning physical removal processes for chloroform is very limited. No data appear to have been reported for dry deposition. A calculated washout ratio of 8.35 at 293 K has been reported (Dana et al. 1985). This washout ratio can be compared to ratios of 10^5 to 10^6 for compounds which are efficiently removed by precipitation events (such as phenol and particles). Since the washout ratio for CHCl_3 is some four to five orders of magnitude less than that corresponding to efficient wet deposition, it is clear that wet deposition of chloroform will be negligible compared with chemical reaction with OH radicals.

E. Atmospheric Formation Processes

No chemical formation processes for CHCl_3 in the atmosphere have been identified.

F. Atmospheric Lifetimes

The presently accepted 12-hr daytime average tropospheric OH radical concentration in the northern and southern hemispheres is $1.5 \times 10^6 \text{ radicals cm}^{-3}$ (Prinn et al. 1987), which is derived from a knowledge of the total worldwide emissions of CH_3CCl_3 and the present atmospheric burden of CH_3CCl_3 . Using this value, and the rate constants given above for 265 K (the "average" temperature of the troposphere) and 298 K, a range of atmospheric lifetimes for chloroform of 150 (assuming a temperature of 298 K) to 233 days (for a temperature of 265 K) is obtained. This is in reasonable agreement with calculated atmospheric

lifetimes of 120 and 180 days reported by Rasmussen et al. (1982) and Khalil et al. (1983), respectively, based upon measurements of the atmospheric concentrations of CHCl_3 and the estimated anthropogenic CHCl_3 emissions into the troposphere.

Clearly, chloroform is a persistent compound in the troposphere, and it will be dispersed from its anthropogenic emission sources not only regionally and over continental distances, but also globally (in agreement with atmospheric measurements).

G. Ambient Concentrations

The average observed concentrations of chloroform in seven U. S. cities in 1980 and 1981 have been reported by Singh et al. (1982) to range from 73 parts per trillion (ppt) in St. Louis to 703 ppt in Riverside, CA. The minimum and maximum concentrations observed in Riverside between July 2-12, 1980 was 109 and 4,750 ppt, respectively. In a separate study, Singh et al. (1981) reported the diurnal variation of chloroform in Phoenix, AZ, to range between ~50 and 330 ppt.

With respect to tropospheric background levels of chloroform, average values of 30 and 19 ppt were reported for 1981 for the northern and southern hemispheres, respectively, leading to a global tropospheric average of 25 ppt (Khalil et al. 1983). No data were given for the rate of increase in the tropospheric background levels of chloroform.

H. Conclusion

The only significant loss process for chloroform in the troposphere is reaction with hydroxyl radicals, leading to a tropospheric lifetime in the range of 150 to 230 days.

I. References

- Atkinson, R. and W. P. L. Carter (1984): Kinetics and mechanisms of the gas-phase reactions of ozone with organic compounds under atmospheric conditions. Chem. Rev., 84, 437-470.
- Atkinson, R. (1986): Kinetics and mechanisms of the gas-phase reactions of the hydroxyl radical with organic compounds under atmospheric conditions. Chem. Rev., 86, 69-201.

- Atkinson, R. (1987): A structure-activity relationship for the estimation of rate constants for the gas-phase reactions of OH radicals with organic compounds. *Int. J. Chem. Kinet.*, 19, 799-828.
- Atkinson, R. (1989): Kinetics and mechanisms of the gas-phase reactions of the hydroxyl radical with organic compounds. *J. Phys. Chem. Ref. Data*, Monograph 1, 1-246.
- Atkinson, R., S. M. Aschmann and J. N. Pitts, Jr. (1988), Rate constants for the gas-phase reactions of the NO₃ radical with a series of organic Compounds at 296 ± 2 K. *J. Phys. Chem.*, 92, 3454-3457.
- Bidleman, T. F. (1988): Atmospheric Processes. *Environ. Sci. Technol.*, 22, 361-367.
- Cooper, R., J. B. Cumming, S. Gordon and W. A. Mulac, (1980): The reactions of the halomethyl radicals CC₁3 and CF₃ with oxygen. *Radiat. Phys. Chem.*, 16, 169-174.
- Cox, R. A., R. G. Derwent, A. E. J. Eggleton and J. E. Lovelock (1976): Photochemical oxidation of halocarbons in the troposphere. *Atmos. Environ.*, 10, 305-308.
- Dana, M. T., R. N. Lee and J. M. Hales (1985): Hazardous air pollutants: Wet removal rates and mechanisms. EPA-600/S3-84-113, January.
- Davis, D. D., G. Machado, B. Conaway, Y. Oh and R. Watson (1976): A temperature dependent kinetics study of the reaction of OH with CH₃Cl, CH₂Cl₂, CHCl₃ and CH₃Br. *J. Chem. Phys.*, 65, 1268-1274.
- DeMore, W. B., J. J. Molina, S. P. Sander, D. M. Golden, R. F. Hampson, M. J. Kurylo, C. J. Howard and A. R. Ravishankara (1987): Chemical Kinetics and Photochemical Data for Use in Stratospheric Modeling. Evaluation Number 8, Jet Propulsion Laboratory, Publication 87-41, September 15.
- Dognon, A. M., F. Caralp and R. Lesclaux (1985): Reactions des radicaux chlorofluoromethyl peroxy avec NO: Etude cinetique dans le domaine de temperature compris entre 230 et 430 K. *J. Chim. Phys.*, 82, 349-352.
- Howard, C. J. and K. M. Evenson (1976): Rate constants for the reactions of OH with CH₄ and fluorine, chlorine and bromine substituted methanes at 296 K. *J. Chem. Phys.*, 64, 197-202.
- Hubrich, C. and F. Stuhl (1980): The ultraviolet absorption spectrum of some halogenated methanes and ethanes of atmospheric interest. *J. Photochem.*, 12, 93-107.
- Jeong, K.-M. and F. Kaufman (1982): Kinetics of the reaction of hydroxyl radical with methane and with nine Cl- and F-substituted methanes. 1. Experimental results, comparisons and applications. *J. Phys. Chem.*, 86, 1808-1815.

- Jeong, K.-M., K.-J. Hsu, J. B. Jeffries and F. Kaufman (1984): Kinetics of the reactions of OH with C_2H_6 , CH_2CCl_3 , $CH_2ClCHCl_2$, $CHClCClF_2$ and CH_2FCF_3 . J. Phys. Chem., 88, 1222-1226.
- Khalil, M. A. K., R. A. Rasmussen and S. D. Hoyt (1983): Atmospheric chloroform ($CHCl_3$): Ocean-air exchange and global mass balance. Tellus, 35B, 266-274.
- Klöpffer, W., R. Frank, E.-G. Kohl and F. Haag (1986): Quantitative erfassung der photochemischen transformationsprozesse in der troposphäre. Chemiker-Zeitung, 110, 57-61.
- Prinn, R., D. Cunnold, R. Rasmussen, P. Simmonds, F. Alyea, A. Crawford, P. Fraser and R. Rosen (1987): Atmospheric trends in methylchloroform and the global average for the hydroxyl radical. Science, 238, 945-950.
- Rasmussen, R. A., M. A. K. Khalil, A. J. Crawford and P. J. Fraser (1982): Natural and anthropogenic trace gases in the southern hemisphere. Geophys. Res. Lett., 9, 704-707.
- Rayez, J. C., M. T. Rayez, P. Halvick, B. Duguay, R. Lesclaux and J. J. Dannenberg (1987): A theoretical study of the decomposition of halogenated alkoxy radicals. I. Hydrogen and chlorine extrusions. Chem. Phys., 116, 203-213.
- Robbins, D. E. (1977): International Conference on Problems Related to the Stratosphere, W. Huntress, Jr. and D. Maple (Eds.), Jet Propulsion Laboratory Publication JPL 77-12.
- Simon, P. C., D. Gillotay, N. Vanlaethem-Meuree and J. Wisenberg. (1988): Ultraviolet absorption cross-sections of chloro and chlorofluoromethanes at stratospheric temperatures. J. Atmos. Chem., 7, 107-135.
- Singh, H. B., L. J. Salas, A. J. Smith and H. Shigeishi (1981): Measurements of some potentially hazardous organic chemicals in urban environments. Atmos. Environ., 15, 601-612.
- Singh, H. B., L. J. Salas and R. E. Stiles (1982): Distribution of selected gaseous organic mutagens and suspect carcinogens in ambient air. Environ. Sci. Technol. 16, 872-880.
- WMO (1986): World Meteorological Organization, Report No. 16, Volume I, Atmospheric Ozone 1985, Global Ozone Research and Monitoring Project.

APPENDIX B

ATMOSPHERIC LIFETIME AND FATE OF 1,3-BUTADIENE

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

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

Roger Atkinson and Arthur M. Winer

October 1988

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

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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 includes:

- Photolysis during daylight hours
- Reaction with the hydroxyl (OH) radical during daylight hours
- Reaction with the hydroperoxyl (HO₂) radical, mainly during afternoon/evening hours
- Reaction with the nitrate (NO₃) radical during nighttime hours
- Reaction with nitrogen dioxide (NO₂)
- Reaction with ozone (O₃)
- Reaction with gaseous nitric acid (HNO₃)

For the great majority of organic compounds, the most important of these remain photolysis and reaction with hydroxyl (OH) and nitrate (NO₃) radicals and with ozone (O₃).

However, for a limited number of organic compounds, one or more of the other reactive chemical species in the troposphere may react with organic compounds at significant rates. For example, HO₂ radicals react with formaldehyde and, more slowly, with acetaldehyde and glyoxal; NO₂ reacts with dialkenes; and gaseous HNO₃ reacts with basic compounds such as the amines.

Additionally, for chemical compounds present in the adsorbed phase, photolysis and reaction with O₃, N₂O₅, NO₂, HNO₃, HONO, H₂SO₄ and hydrogen peroxide (H₂O₂) 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).

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

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

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

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

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

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

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

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

In this report, we describe the available literature data concerning the chemical and physical removal processes for 1,3-butadiene ($\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$) and estimate its resulting atmospheric lifetime. We will also summarize the atmospheric chemistry of this compound. Since 1,3-butadiene is gaseous under atmospheric conditions, we consider only the gas-phase processes.

B. Chemical Loss Processes

1. Ozone

Kinetic data for the gas-phase reaction of ozone with 1,3-butadiene have been obtained by Hanst et al. (1958), Japar et al. (1974), Becker et al. (1974), Toby and Toby (1975) and Bahta et al. (1984), and these data are given in Table 1. The data from all these studies are in reasonable agreement. Since the individual rate constants at the temperatures studied were not given by Becker et al. (1974) or Toby and Toby (1975), a least-squares analysis of the entire data set cannot be carried out. A unit-weighted average of the room temperature rate constants of Hanst et al. (1958), Japar et al. (1974), Becker et al. (1974) and Bahta et al. (1984) [neglecting the rate constant study of Toby and Toby (1975) because of the magnitude of the error limits associated with it] leads to

$$k(\text{O}_3 + 1,3\text{-butadiene}) = 7.4 \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

Combining this 298 K rate constant with a temperature dependence of $B = 2500 \text{ K}$ derived from the temperature dependencies of Becker et al. (1974) and Bahta et al. (1984) leads to the recommendation of

$$k(\text{O}_3 + 1,3\text{-butadiene}) = 3.26 \times 10^{-14} e^{-2500/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}.$$

At 265 K (the average temperature of the troposphere), the rate constant is $2.6 \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

Table 1. Reported Rate Constants k and Arrhenius Parameters, $k = Ae^{-B/T}$, for the Reaction of O_3 with 1,3-Butadiene

| A (cm^3 molecule ⁻¹ s ⁻¹) | B (K) | $10^{18} \times k$ (cm^3 molecule ⁻¹ s ⁻¹) | At T (K) | Technique | Reference | Temperature Range Covered (K) |
|---|----------------|--|-------------|-----------|----------------------|-------------------------------------|
| | | | a | F/S-IR | Hanst et al. (1958) | |
| | | 8.1 | | | | |
| | | 8.4 ± 0.2 | 299 ± 2 | S-CL | Japar et al. (1974) | |
| 5.45×10^{-14} | 2682 ± 101 | 6.7^b | 298 | S-UV | Becker et al. (1974) | $\sim 286-358^c$ |
| 1.05×10^{-13} | 2919 ± 403 | 7.5 ± 1.3^d | 303 | S-UV | Toby and Toby (1975) | 273-343 |
| 2.20×10^{-14} | 2430 ± 55 | 6.3^b | 298 | S-UV | Bahta et al. (1984) | 254-299 |

^aRoom temperature.

^bCalculated from the Arrhenius expression.

^cDerived from graphical tabulations given.

^dValue cited by Toby et al. (1976).

2. OH Radicals

The available kinetic data of Lloyd et al. (1976), Atkinson et al. (1977), Barnes et al. (1982), Ohta (1983), Atkinson and Aschmann (1984) and Liu et al. (1988) are given in Table 2 and are plotted in Arrhenius form in Figure 1 [both adapted from Atkinson (1989)]. It can be seen that the room temperature rate constants from the studies of Lloyd et al. (1976), Atkinson et al. (1977), Barnes et al. (1982), Ohta (1983), Atkinson and Aschmann (1984) and Liu et al. (1988) are in very good agreement. Furthermore, the temperature dependencies obtained by Atkinson et al. (1977) and Liu et al. (1988) are in good agreement.

A unit-weighted least-squares analysis of the absolute rate constant data of Atkinson et al. (1977) and Liu et al. (1988) at temperatures <500 K yields the Arrhenius expression of

$$k(1,3\text{-butadiene}; T < 500 \text{ K}) = (1.44^{+0.54}_{-0.40}) \times 10^{-11} e^{(448 \pm 117)/T} \\ \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature 299-483 K, where the indicated errors are two least-squares standard deviations. The relative rate data of Atkinson and Aschmann (1984) for a series of alkenes and dialkenes, when combined with the literature absolute rate constants (Atkinson 1989), leads to the recommendation of

$$k(1,3\text{-butadiene}) = 6.78 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

at 295 K. Combined with the above temperature dependence, this yields the recommended Arrhenius expression of

$$k(1,3\text{-butadiene}; T < 500 \text{ K}) = (1.48^{+0.56}_{-0.42}) \times 10^{-11} e^{(448 \pm 117)/T} \\ \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 295-483 K, where the indicated errors are two least-squares standard deviations, and

$$k(1,3\text{-butadiene}) = 6.66 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K},$$

Table 2. Rate Constants k and Arrhenius Parameters ($k = Ae^{-B/T}$) for the Gas-Phase Reactions of the OH Radical with 1,3-Butadiene

| $10^{12} \times A$ ($\text{cm}^3 \text{ mole}^{-1} \text{ s}^{-1}$) | B (K) | $10^{12} \times k$ ($\text{cm}^3 \text{ mole}^{-1} \text{ s}^{-1}$) | at T (K) | Technique | Reference | Temperature range covered (K) |
|--|----------------|--|-------------------------|--|------------------------------|-------------------------------|
| | | 67.6 ± 13.6 | 305 ± 2 | RR [relative to k(n-butane) = 2.62×10^{-12}] ^a | Lloyd et al. (1976) | |
| 14.5 | -468 ± 151 | 68.5 ± 6.9 57.2 ± 5.7 43.3 ± 4.4 | 299.5 347.2 424.0 | FP-RF | Atkinson et al. (1977) | 299-424 |
| | | 65.0 | 300 | RR [relative to k(ethene) = 8.44×10^{-12}] ^a | Barnes et al. (1982) | |
| | | 61.6 ± 1.5 | 297 ± 2 | RR [relative to k(propene) = 2.65×10^{-11}] ^a | Ohta (1983) | |
| | | 68.8 ± 2.2 | 297 ± 2 | RR [relative to k(2-methyl-2-butene) = 8.72×10^{-11}] ^a | Ohta (1983) | |
| | | 67.8 ± 2.2 | 295 ± 1 | RR [relative to k(propene) = 2.68×10^{-11}] ^a | Atkinson and Aschmann (1984) | |

Table 2 (continued) - 2

| $10^{12} \times A$ ($\text{cm}^3 \text{ mole}^{-1} \text{ s}^{-1}$) | B (K) | $10^{12} \times k$ ($\text{cm}^3 \text{ mole}^{-1} \text{ s}^{-1}$) | at T (K) | Technique | Reference | Temperature range covered (K) |
|--|----------|--|----------|-----------|-------------------|-------------------------------|
| 14 ± 1 -440 \pm 40 (313-623 K) | | 61 \pm 6 | 313 | PR-RA | Liu et al. (1988) | 313-1203 |
| | | 50 \pm 5 | 333 | | | |
| | | 51 \pm 5 | 338 | | | |
| | | 46 \pm 5 | 373 | | | |
| | | 41 \pm 4 | 393 | | | |
| | | 47 \pm 5 | 408 | | | |
| | | 42 \pm 4 | 438 | | | |
| | | 35 \pm 4 | 483 | | | |
| | | 29 \pm 3 | 563 | | | |
| | | 30 \pm 3 | 623 | | | |
| | | 30 \pm 3 | 673 | | | |
| | | 24 \pm 3 | 723 | | | |
| | | 20 \pm 2 | 773 | | | |
| | | 17 \pm 2 | 873 | | | |
| | | 15 \pm 2 | 923 | | | |
| | | 11 \pm 1 | 1023 | | | |
| | | 10 \pm 1 | 1053 | | | |
| | | 6.5 \pm 0.6 | 1153 | | | |
| | | 6.9 \pm 0.7 | 1173 | | | |
| | | 7.7 \pm 0.8 | 1203 | | | |

^aRate constant recommendations taken from Atkinson (1989).

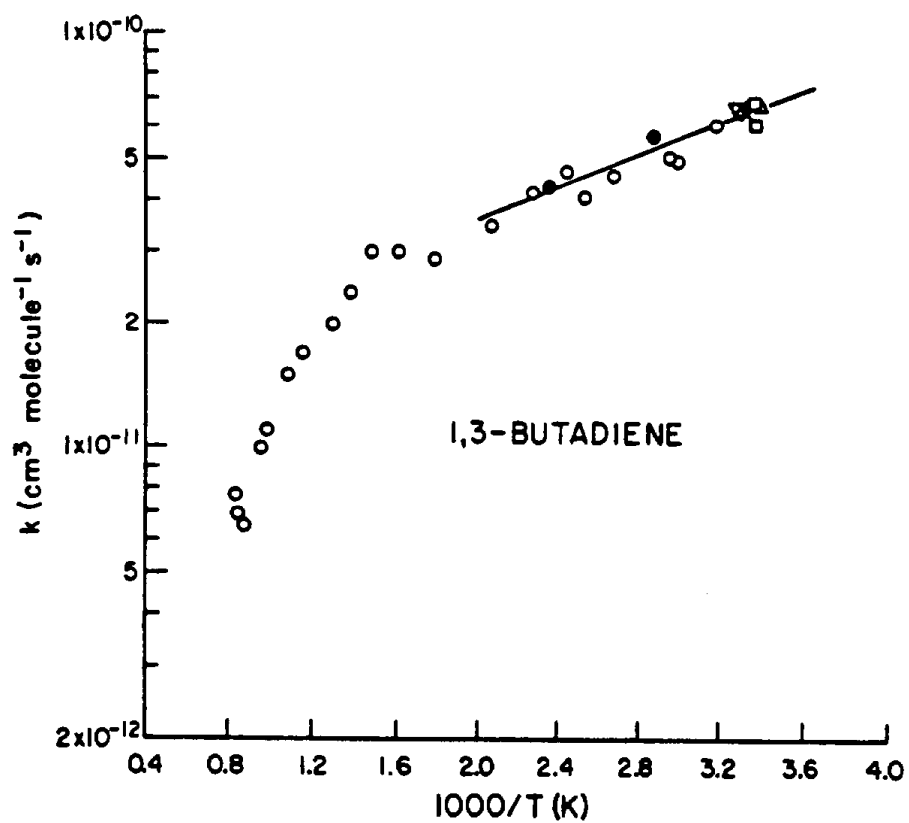


Figure 2. Arrhenius plot of rate constants for the reaction of the OH radical with 1,3-butadiene. (∇) Lloyd et al. (1976); (\bullet) Atkinson et al. (1977); (x) Barnes et al. (1982); (\square) Ohta (1983); (Δ) Atkinson and Aschmann (1984); (\circ) Liu et al. (1988); (—) recommendation (see text).

with an estimated overall uncertainty at 298 K of $\pm 20\%$. Using the Arrhenius expression given above, the OH rate constant at 265 K is $8.03 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

The relative rate constants of Lloyd et al. (1976), Barnes et al. (1982) and Ohta (1983) are in very good agreement with this recommendation.

By analogy with the alkenes such as ethene, propene and the butenes, this rate constant is that for the OH radical addition pathway and will be very close to the high-pressure limit, at least up to ~ 500 K. Indeed, the above recommendation (Atkinson 1989) provides a good fit to the rate constants measured by Liu et al. (1988) in one atmosphere of argon diluent up to ~ 700 K.

3. NO₃ Radicals

Kinetics data for the reaction of NO₃ radicals with 1,3-butadiene have been obtained by Canosa-Mas et al. (1988), Rahman et al. (1988) and Atkinson et al. (1988), and these data are summarized in Table 3. The recommended rate constant of

$$k(1,3\text{-butadiene}) = (1.0 \pm 0.2) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K}$$

for the reaction of NO₃ radicals with 1,3-butadiene is based upon the study of Atkinson et al. (1988).

4. Other Chemical Species

Based on chemical considerations, none of the other reactive species present in the troposphere (cited in the Introduction) are expected to react with 1,3-butadiene, certainly not at rates which are significant relative to its rate of reaction with OH and NO₃ radicals or with ozone.

5. Photolysis

1,3-Butadiene will not undergo photolysis in the actinic region, since it does not absorb radiation above ~ 230 nm (Calvert and Pitts 1966).

C. Physical Loss Processes

No data concerning the physical removal processes for 1,3-butadiene are available. However, neither wet nor dry deposition is expected to be

Table 3. Room Temperature Rate Constants for the Gas-Phase Reaction of the NO₃ Radical with 1,3-Butadiene

| $k(\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1})$ | Reference |
|---|--------------------------|
| $(2.2 \pm 0.6) \times 10^{-13}$ | Canosa-Mas et al. (1988) |
| $(1.7 \pm 0.3) \times 10^{-13}$ | Rahman et al. (1988) |
| $(9.79 \pm 1.17) \times 10^{-14}$ | Atkinson et al. (1988) |

important as a loss process compared with the chemical reactions with OH and NO₃ radicals and O₃.

D. Atmospheric Formation Processes

No chemical formation processes for 1,3-butadiene in the atmosphere have been identified.

E. Atmospheric Lifetimes

The rate constants cited above for the gas-phase reactions of OH and NO₃ radicals and O₃ with 1,3-butadiene can be combined with measured or estimated ambient atmospheric concentrations of OH and NO₃ radicals and O₃ to calculate the atmospheric lifetimes of 1,3-butadiene with respect to these potential gas-phase reactions. For this purpose, we use ambient atmospheric concentrations of $1.5 \times 10^6 \text{ molecule cm}^{-3}$ for OH radicals during a 12-hr daytime period (Prinn et al. 1987) [an average tropospheric concentration for the northern and southern hemispheres derived from a knowledge of the total worldwide emissions of CH₃CCl₃ and the present atmospheric burden of CH₃CCl₃], $2.4 \times 10^8 \text{ molecule cm}^{-3}$ for NO₃ radicals during a 12-hr nighttime period (Platt et al. 1984, Atkinson et al. 1986) and $7 \times 10^{11} \text{ molecule cm}^{-3}$ for O₃ during a complete 24-hr day (Logan 1985). The calculated lifetimes due to these gas-phase reactions are given in Table 4.

From these calculated atmospheric lifetimes, it is clear that reaction with O₃ will be a minor reaction pathway for 1,3-butadiene and that reaction with OH radicals during the day and with NO₃ radicals at

Table 4. Calculated Atmospheric Lifetimes of 1,3-Butadiene with Respect to Gas-Phase Reaction with OH and NO₃ Radicals and O₃

| Reaction with | At Temperature T (K) | Lifetime τ |
|------------------------------|-------------------------|----------------------|
| OH ^a | 265 298 | 2.3 hr 2.8 hr |
| NO ₃ ^b | 298 | 12 hr |
| O ₃ ^c | 265 298 | 6.4 days 2.2 days |

^aFor a 12-hr average daytime OH radical concentration of 1.5×10^6 molecule cm⁻³ (Prinn et al. 1987).

^bFor a 12-hr average nighttime NO₃ radical concentration of 2.4×10^8 molecule cm⁻³ (Platt et al. 1984, Atkinson et al. 1986).

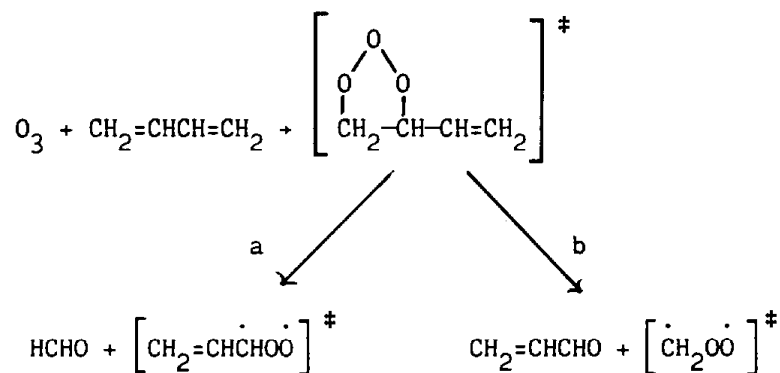
^cFor a 24-hr average O₃ concentration of 7×10^{11} molecule cm⁻³ [30 ppb] (Logan 1985).

night will be the dominant removal pathways for this reactive compound. Clearly, 1,3-butadiene will be of importance only close to its emission sources and within the airshed in which it is emitted.

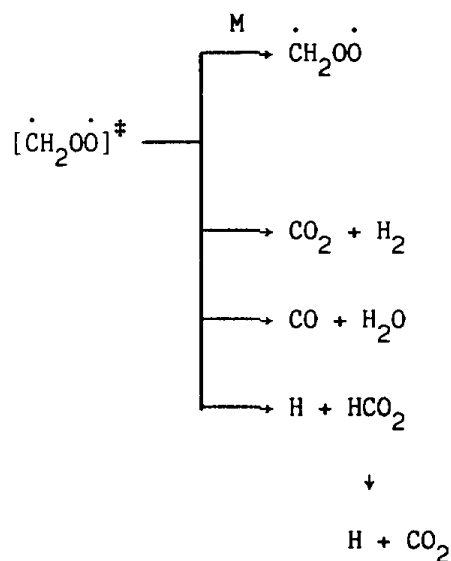
F. Atmospheric Reactions

1. Reaction with O₃

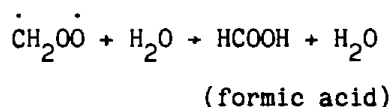
As discussed by Atkinson and Carter (1984), the gas-phase reaction of O₃ with 1,3-butadiene involves initial addition to form an energy-rich "molozonide", which is then expected to decompose rapidly



with the relative importance of pathways (a) and (b) not being known. The initially energy-rich $[\dot{\text{C}}\text{H}_2\dot{\text{O}}\text{O}]^\ddagger$ biradical can be collisionally thermalized or decompose (Atkinson and Carter 1984):



with the thermalized biradical $\dot{\text{C}}\text{H}_2\dot{\text{O}}\text{O}$ reacting predominantly with water vapor under atmospheric conditions:

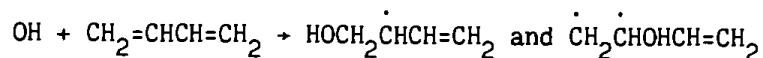


The fate of the $[\text{CH}_2=\text{CH}\dot{\text{C}}\text{HO}\text{O}]^\ddagger$ biradical is not presently known.

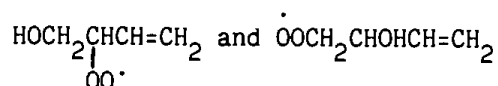
Thus, the available data suggest that the major products of the O_3 reaction with 1,3-butadiene will be formaldehyde (HCHO) and acrolein ($\text{CH}_2=\text{CHCHO}$), together with products including formic acid (HCOOH), CO, CO_2 , H_2 , and HO_2 radicals, which arise from subsequent reactions of the "Criegee" biradicals.

2. OH Radical Reaction

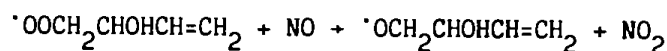
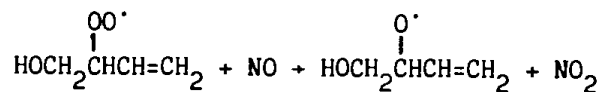
Under atmospheric conditions, the reaction of the OH radical with 1,3-butadiene proceeds essentially entirely (>99%) by initial OH radical addition (Atkinson 1989)



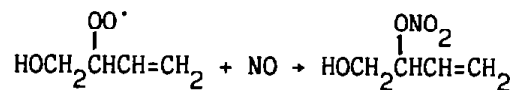
These initially formed radicals will rapidly (in $\leq 1\mu\text{s}$) add O_2 to yield the peroxy radicals



In the presence of NO , these peroxy radicals are expected to yield NO_2 and the corresponding alkoxy radical,

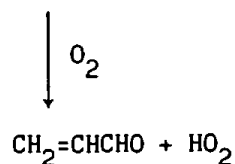
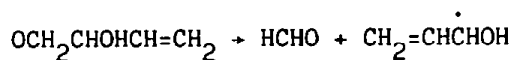
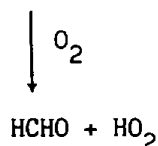
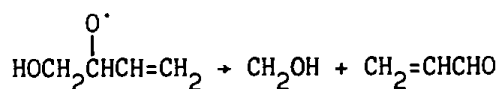


although it is possible that a small amount ($\leq 5\%$) of an organic nitrate may be formed. For example



Under conditions where the NO mixing ratios are ≤ 30 parts-per-trillion, the above peroxy radicals will react with HO_2 (to form hydroperoxides, ROOH) and/or other peroxy radicals (to form, at least in part, the above alkoxy radicals) in competition with the reactions with NO given above.

The alkoxy radicals shown above are expected to decompose rapidly.

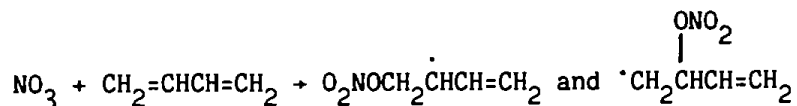


Thus, in the presence of NO the major products are expected to be HCHO and $\text{CH}_2=\text{CHCHO}$, and this is observed. Thus, Heuss and Glasson (1968) obtained ~37-40% yields of HCHO and $\text{CH}_2=\text{CHCHO}$ (uncorrected for losses) in an irradiated NO-1,3-butadiene-air mixture. However, furan



has been observed as a minor product (~4-6%) from the OH radical reaction with 1,3-butadiene, both in the presence and absence of NO (Ohta 1984, Atkinson et al. 1989).

NO₃ Radical Reaction. As for the OH radical reaction, the NO₃ radical reaction proceeds by initial addition



This radical will rapidly add O₂, and the resulting peroxy radicals are then expected to react to HO₂ radicals and/or other peroxy radicals. However, the reaction mechanisms and products formed from these reactions are as yet unknown.

G. Ambient Concentrations

Although high resolution gas chromatograms exhibiting evidence of trace amounts of 1,3-butadiene in urban air have been reported in the literature (Matuska et al. 1986), we have not found any quantitative data for the atmospheric concentrations of this compound published in the past decade.

H. Conclusion

1,3-Butadiene will be removed from the atmosphere both by gas-phase reaction with OH radicals during the day and with NO₃ radicals at night, with calculated atmospheric lifetimes of a few hours and half a day, respectively, for the two processes. Thus, 1,3-butadiene will be confined to a local radius of impact largely within the airshed in which it is emitted.

I. References

- Atkinson, R., R. A. Perry and J. N. Pitts, Jr. (1977) Absolute rate constants for the reaction of OH radicals with allene, 1,3-butadiene and 3-methyl-1-butene over the temperature range 299-424 K. J. Chem. Phys., 67, 3170-3174.
- Atkinson, R. and S. M. Aschmann (1984) Rate constants for the reaction of OH radicals with a series of alkenes and dialkenes at 295 ± 1 K. Int. J. Chem. Kinet., 16, 1175-1186.
- Atkinson, R. and W. P. L. Carter (1984) Kinetics and mechanisms of the gas-phase reactions of ozone with organic compounds under atmospheric conditions. Chem. Rev., 84, 437-470.
- Atkinson, R., A. M. Winer and J. N. Pitts, Jr. (1986) Estimation of night-time N₂O₅ concentrations from ambient NO₂ and NO₃ radical concentrations and the role of N₂O₅ in night-time chemistry. Atmos. Environ., 20, 331-339.
- Atkinson, R., S. M. Aschmann and J. N. Pitts, Jr. (1988) Rate constants for the gas-phase reactions of the NO₃ radical with a series of organic compounds at 296 ± 2 K. J. Phys. Chem., 92, 3454-3457.
- Atkinson, R. (1989) Kinetics and mechanisms of the gas-phase reactions of the hydroxyl radical with organic compounds. J. Phys. Chem. Ref. Data, Monograph 1, 1-246.

- Atkinson, R., S. M. Aschmann, E. C. Tuazon, J. Arey and B. Zielinska (1989) Formation of 3-methylfuran from the gas-phase reaction of OH radicals with isoprene and the rate constant for its reaction with the OH radical. *Int. J. Chem. Kinet.*, 21, 593-604.
- Bahta A., R. Simonaitis and J. Heicklen (1984) Reactions of ozone with olefins: Ethylene, allene, 1,3-butadiene and trans-1,3-pentadienes. *Int. J. Chem. Kinet.*, 16, 1227-1246.
- Barnes, I., V. Bastian, K. H. Becker, E. H. Fink and F. Zabel (1982) Reactivity studies of organic substances towards hydroxyl radicals under atmospheric conditions. *Atmos. Environ.*, 16, 545-550.
- Becker, K. H., U. Schurath and H. Seitz (1974) Ozone-olefin reactions in the gas phase. I. Rate constants and activation energies. *Int. J. Chem. Kinet.*, 6, 725-739.
- Bidleman, T. F. (1988) Atmospheric processes. *Environ. Sci. Technol.*, 22, 361-367.
- Calvert, J. G. and J. N. Pitts, Jr. (1966) "Photochemistry," New York, NY.
- Canosa-Mas, C., S. J. Smith, S. Toby and R. P. Wayne (1988) Reactivity of the nitrate radical towards alkynes and some other molecules. *J. Chem. Soc., Faraday Trans. 2*, 84, 247-262.
- Hanst, P. L., E. R. Stephens, W. E. Scott and R. C. Doerr (1958) Atmospheric Ozone-Olefin Reactions. Franklin Institute Press: Philadelphia, PA, August.
- Heuss, J. M. and W. A. Glasson (1968) Hydrocarbon reactivity and eye irritation. *Environ. Sci. Technol.*, 2, 1109-1116.
- Japar, S. M., C. H. Wu, and H. Niki (1974) Rate constants for the reaction of ozone with olefins in the gas phase. *J. Phys. Chem.*, 78, 2318-2320.
- Liu, A., W. A. Mulac and C. D. Jonah (1988) Rate constants for the gas-phase reactions of OH radicals with 1,3-butadienes and allene at 1 atm in Ar and over the temperature range 305-1173 K. *J. Phys. Chem.*, 92, 131-134.
- Lloyd, A. C., K. R. Darnall, A. M. Winer and J. N. Pitts, Jr. (1976) Relative rate constants for reaction of the hydroxyl radical with a series of alkanes, alkenes and aromatic hydrocarbons. *J. Phys. Chem.*, 80, 789-794.
- Logan, J. A. (1985) Tropospheric ozone: Seasonal behavior, trends and anthropogenic influence. *J. Geophys. Res.*, 90, 10463-10482.
- Matuska, P., M. Koval and W. Seiler (1986) A high resolution GC-analysis method for determination of C₂-C₁₀ hydrocarbons in air samples. *J. High Res. Chromat. & Chromat. Comm.*, 9, 577-583.

- Ohta, T. (1983) Rate constants for the reactions of OH radicals in the gas phase. Estimate of rate constants from those for mono-olefins. J. Chem. Phys., 87, 1209-1213.
- Ohta, T. (1984) Furan ring formation in OH-initiated photooxidation of 1,3-butadiene and cis-1,3-pentadiene. Bull. Chem. Soc. Jpn., 57, 960-966.
- Platt, U. F., A. M. Winer, H. W. Biermann, R. Atkinson and J. N. Pitts, Jr. (1984) Measurement of nitrate radical concentrations in continental air. Environ. Sci. Technol., 18, 365-369.
- Prinn, R., D. Cunnold, R. Rasmussen, P. Simmonds, F. Alyea, A. Crawford, P. Fraser and R. Rosen (1987) Atmospheric trends in methylchloroform and the global average for the hydroxyl radical. Science, 238, 945-950.
- Rahman, M. M., E. Becker, Th. Benter and R. N. Schindler (1988) A gas phase kinetic investigation of the system $F + HNO_3$ and the determination of absolute rate constants for the reaction of the NO_3 radical with CH_3SH , 2-methylpropene, 1,3-butadiene and 2,3-dimethyl-2-butene. Ber. Bunsenges Phys. Chem., 92, 91-100.
- Toby, F. S. and S. Toby (1975) The reaction of ozone with 1,3-butadiene and with allene. Int. J. Chem. Kinet., Symp. 1, 197-204.
- Toby, F. S., S. Toby and H. E. O'Neal (1976) The kinetics of the gas-phase reaction between ozone and alkenes. Int. J. Chem. Kinet., 8, 25-35

APPENDIX C

ATMOSPHERIC LIFETIME AND FATE OF BENZO[A]PYRENE

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

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

Roger Atkinson and Janet Arey

January 1989

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

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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 includes:

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

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

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

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

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

as wet deposition. Our current understanding of these processes, which are dynamic in nature, must be considered to be semi-quantitative at the present time, and in general there is a lack of experimental data concerning these processes for most organic compounds (Bidleman, 1988).

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

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

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

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

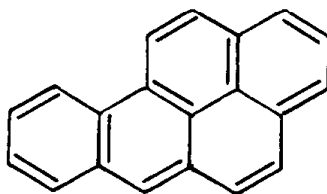
where $\tau_{\text{photolysis}}$, τ_{OH} , τ_{NO_3} and τ_{O_3} are the lifetimes with respect to photolysis, reaction with the OH radical, reaction with the NO_3 radical, and reaction with O_3 , respectively. In turn, these reactive loss processes are determined by the rate constants, k_x , for reaction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

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

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

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

In this report, we describe the available literature data concerning the physical and chemical removal processes for benzo[a]pyrene:



Benzo[a]pyrene (BaP) is a member of the chemical class known as polycyclic (or polynuclear) aromatic hydrocarbons (PAH), which are formed in combustion systems at high temperatures (Bockhorn et al., 1982; Prado et al., 1985; Toqan et al., 1985; Kittelson et al., 1985) and hence are emitted from essentially all combustion sources. In addition to being present in combustion emissions, including cigarette smoke, BaP is also found in fossil fuels (IARC, 1983). BaP has been shown to be carcinogenic to experimental animals (IARC, 1983).

BaP has a vapor pressure at 298 K (room temperature) of 5.6×10^{-9} torr (Yamasaki et al., 1984) and because of this low vapor pressure [which would lead to a maximum mixing ratio in the gas phase of 0.008 parts-per-billion (ppb)] BaP is expected to exist in the atmosphere in the adsorbed phase. No evidence for "blow-off" of BaP from filters onto downstream solid adsorbent traps has been seen (Arey et al., 1987; Coutant et al., 1988), nor has vapor phase BaP been observed (Coutant et al., 1988). Thus, atmospheric BaP is particle-associated and gas-phase reactions of BaP are of no importance. The processes to be considered are then

- Physical loss processes for the particles on which, or in which, BaP resides.
- Adsorbed-phase reactions of BaP on the particles.

B. Physical Loss Processes

The particles with which BaP 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 BaP is associated generally exhibit a particle size range of $<3 \mu\text{m}$ (Pierce and Katz, 1975) and hence the atmospheric lifetime of these particles due to dry deposition is expected to be of the order of 10 days.

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

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

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

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

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

Thus, considering only its physical atmospheric removal processes, the lifetime of BaP due to particle dry deposition is expected to be around 10 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 (μm) | Lifetime (days) |
|----------------------------|-----------------|
| 0.002 | 0.01 |
| 0.02 | 1 |
| 0.2 | 10 |
| 2 | 10 |
| 20 | 1 |
| 200 | 0.01 |

C. Chemical Loss Processes

In addition to the physical removal of the particles with which the BaP is associated, the BaP can also be transformed by a number of chemical processes in the adsorbed phase. These include photolysis and reaction with O_3 , SO_2 , NO_2 and/or HNO_3 and N_2O_5 , and a large number of experimental investigations of these potential reaction pathways have been carried out (see, for example, Pitts et al., 1978, 1980, 1985, 1986; Katz et al., 1979; Jäger and Hanus, 1980; Korfmacher et al., 1980; Peters and Seifert, 1980; Butler and Crossley, 1981; Blau and Güsten, 1981; Grosjean et al., 1983; Brorström et al., 1983; Van Vaeck and Van Cauwenberghe, 1984; Behymer and Hites, 1985, 1988; Brorström-Lundén and Lindskog, 1985; Kamens et al., 1985, 1986, 1988; Lindskog et al., 1985; Yokley et al., 1985, 1986; Güsten, 1986; Valerio et al., 1987; Arey et al., 1988; Coutant et al., 1988; Nielsen, 1988). Interpretation of the experimental data obtained from the laboratory studies is rendered difficult due to the diverse substrates used, and in many cases conflicting data have been obtained. As discussed below, some differences may be attributed to the availability of the BaP for reaction, i.e., whether it was present as an adsorbed surface layer or included in the particles, or whether the particles were "freshly" emitted or were "aged" particles.

Reaction with O_3 . The results obtained concerning the stability of BaP adsorbed onto surfaces in the presence of O_3 are disparate. Thus, Katz and coworkers (Katz et al., 1979) and Peters and Seifert (1980) observed that BaP reacted in the presence of ambient levels of O_3 , and Pitts et al. (1980) identified the BaP-4,5-epoxide as a product of the reaction of O_3 with BaP deposited onto glass fiber filters. These studies indicated a BaP lifetime with respect to reaction with O_3 (at ambient concentrations, i.e., levels reached in polluted atmospheres) of the order of an hour. In contrast, Grosjean et al. (1983) observed no loss of BaP, either deposited onto blank filters or on filters coated with ambient particles, fly ash or diesel particles, when exposed to 100 ppb of ozone for three hours. Brorström et al. (1983) observed no definitive evidence for losses of BaP (or other PAH) under high-volume sampling conditions with the addition of 200 ppb of O_3 . However, it should be noted that in this latter study, no BaP was added to the ambient particles.

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

These data are generally consistent with the fact that BaP reacts with O_3 , providing that the BaP is available for reaction. This is suggested by the often initially rapid BaP degradation followed by significantly slower BaP losses (Pitts et al., 1986; Coutant et al., 1988). Those experiments in which BaP was coated or deposited onto surfaces should then exhibit reactive losses of BaP, as generally observed (Katz et al., 1979; Peters and Seifert, 1980; Pitts et al., 1980, 1986). Fresh diesel particles (Van Vaeck and Van Cauwenberghe, 1984) and ambient particles collected near a freeway (Pitts et al., 1986) also showed BaP losses upon exposure to O_3 . In contrast, BaP included in particles, as may be expected to be the case for aged particulate matter or particles to which condensation of secondary aerosol has occurred (expected to be the case in urban atmospheres), will not be available for reaction with gaseous ozone and hence under these conditions BaP will be observed to be nonreactive (Brorström et al., 1983; Coutant et al., 1988).

Reaction with Oxides of Nitrogen. A number of studies have been carried out to investigate the reaction of BaP when BaP-associated particles are exposed to oxides and oxyacids of nitrogen (Pitts et al., 1978, 1985; Jäger and Hanus, 1980; Butler and Crossley, 1981; Grosjean et al., 1983; Brorström et al., 1983; Ramdahl et al., 1984; Yokley et al., 1985; Lindskog et al., 1985; Brorström-Lundén and Lindskog, 1985; Kamens et al., 1986; Arey et al., 1988). Although all of these studies observed losses of BaP and, generally, formation of nitro-BaP upon exposure of BaP-containing particles to NO_2 and/or HNO_3 , the data reported are conflicting as to whether NO_2 or HNO_3 is the reactive species. In recent studies in which HNO_3 was removed from the NO_2 exposure gas, no reaction of adsorbed BaP with NO_2 was observed (Grosjean et al., 1983; Yokley et al., 1985). In contrast, Lindskog et al. (1985) did not detect any reaction of BaP on soot with $HONO$ or HNO_3 , but did observe reaction with NO_2 and $NO_2 + HNO_3$ mixtures. In this latter study, the buffering effect of the soot may have played a role, and oxy- rather than nitro-PAH derivatives were generally observed as products.

It seems likely that HNO_3 is a nitrating agent for adsorbed BaP, and that NO_2 without HNO_3 will not react. Whether the HNO_3 acts as a catalyst for reaction by NO_2 or is the sole nitrating agent has not been resolved. These BaP reactions are substrate dependent (Jäger and Hanus, 1980;

Ramdahl et al., 1984; Yokley et al., 1985) and, as noted above for the O_3 reactions, presumably require that the BaP be accessible for reaction.

In those studies in which several PAH were examined, the formation of the nitro-derivatives followed the reactivity ranking of the PAH toward electrophilic nitration (Nielsen, 1984). According to Nielsen's ranking, BaP and anthracene are in the same reactivity grouping and more reactive than benz[a]anthracene and pyrene, which in turn are more reactive than benzo[e]pyrene and chrysene with, finally, fluoranthene, phenanthrene and naphthalene being the least reactive of the PAH commonly found in ambient air. The presence of nitro-BaP in combustion emissions (Gibson, 1982, 1983; Paputa-Peck et al., 1983) is consistent with the high reactivity of BaP toward electrophilic nitration, and its presence in ambient air (Gibson, 1982; Wise et al., 1985) may be due to these combustion emissions.

In ambient air, NO_2 and HNO_3 will both be present. Recently, Arey et al. (1988) studied the disappearance of BaP-d₁₂, adsorbed onto ambient particles, and the formation of nitro-BaP-d₁₁ under high-volume sampling conditions during a wintertime high- NO_x (maximum NO_x concentrations approximately 1 ppm) pollution episode in the Los Angeles air basin. BaP-d₁₂ losses of ~40% were observed during the daylight sampling period on one of the two days, and 6-nitro-BaP-d₁₁ was observed as a product in ~0.01% yield during the 12-hr sampling periods. Thus, the formation of 6-nitro-BaP under ambient conditions is likely to be unimportant, especially if most of the ambient particle-adsorbed BaP is unavailable for reaction.

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

Kamens et al. (1988) observed that the BaP photolysis rate (on freshly generated wood and gasoline combustion soot) depended on the

temperature and ambient water concentration, with a BaP lifetime at 293 K and ~50% relative humidity at midday of ~1 hr. In contrast, for dark fly ashes, half-lives on the order of several days were observed (Behymer and Hites, 1988). Once again it can be concluded that BaP is reactive, and thus may be expected to photolyze in ambient atmospheres, but the extent to which this occurs will depend on the exact nature of the BaP adsorbed state.

Ambient Air Data. Further information concerning the atmospheric reactions and lifetimes of BaP arises from ambient air data. Arey et al. (1988) have shown that under wintertime high- NO_x conditions in southern California (with mid-day temperatures attaining 95 °F) losses of BaP-d₁₂ during 12-hr sampling periods were $\leq 40\%$, and nitration of BaP-d₁₂ was of negligible importance. Losses of particle-incorporated BaP would, presumably, have been lower. From an analysis of ambient air and combustion emissions data, Schuetzle and Frazier (1986) found that the benzo[e]pyrene/benzo[a]pyrene ratio (BeP/BaP) in ambient air of ~1.8 was very similar to the ratio observed in emission sources. Since BaP is much more reactive than BeP toward electrophilic reaction (Nielsen, 1984), reaction with O_3 (Van Vaeck and Van Cauwenberghe, 1984) and photolysis (Behymer and Hites, 1988), this observation suggests that once the BaP and BeP are adsorbed on particles they do not undergo significant degradation in the atmosphere.

Nielsen (1988) investigated the dependence of the BaP/BeP ratio on the wind direction, and hence the vicinity of the source, in Denmark. Higher BeP concentrations were associated with local sources, and the BaP/BeP ratio was found to correlate with the BeP concentration, suggesting that BaP was being degraded in the atmosphere. The author concluded that the BaP decay rate was relatively fast (Nielsen, 1988).

Atkinson et al. (1988) measured PAH and PAH-derivatives at seven sites throughout California. Consistent with the work of Nielsen (1988), the sites with the highest BaP/BeP ratios, Mammoth Lakes (BaP/BeP = 1.5) and Concord (BaP/BeP = 1.3), also had the highest BeP concentrations. Furthermore the BaP/BeP ratio was lowest at Glendora (BaP/BeP = 0.35) a site where significant atmospheric reaction had occurred, as evidenced by the formation of 2-nitropyrene from pyrene (Atkinson et al., 1988). (For a complete discussion of the PAH transformations in the atmospheres

sampled see Section X of Atkinson et al., 1988.) The apparent inconsistency in the data of Schuetzle and Frazier (1986) and those of Nielsen (1988) and Atkinson et al. (1988) probably reflects differences due to comparisons of averaged values from generally aged emissions (Schuetzle and Frazier, 1986) versus BaP concentrations resulting from a single emission source (such as wood smoke at Mammoth Lakes) and/or fresh emissions (Nielsen, 1988; Atkinson et al., 1988).

Although it is difficult to estimate a lifetime for BaP from these laboratory and ambient air data, it must be concluded that, due to chemical reaction and/or photolysis, the lifetime of whatever fraction of the BaP is available for reaction is on the order of a few hours in polluted urban atmospheres during summertime. This lifetime will depend on the nature (chemical reactivity) of the atmosphere into which the BaP is emitted. For BaP within the particles and unavailable for reaction, or BaP stabilized due to adsorption, the expected particle lifetimes leads to an atmospheric lifetime of BaP of ≤ 10 days due to dry deposition of the particles.

D. Atmospheric Formation Processes

There are no atmospheric formation pathways for BaP. As mentioned in the Introduction, BaP is present in essentially all combustion systems. These combustion sources of BaP include emissions from automobiles, industrial processes, domestic heating systems, waste incineration facilities, tobacco smoking, agricultural burns and several natural sources, including forest fires and volcanic eruptions (Nikolaou et al., 1984).

E. Atmospheric Concentrations in California

Recently the California Air Resources Board has funded studies which included the measurement of ambient BaP concentrations at several locations in California (Flessel et al., 1984; Winer et al., 1987; Atkinson et al., 1988). The BaP data from these studies for sampling sites in Richmond, Martinez, Concord, Pittsburg, Claremont, Torrance, Glendora, Yuba City, Mammoth Lakes, Oildale, Reseda, Pt. Arguello and San Nicolas Island are given in Tables 2-4. Where available, the BeP concentration data are also given. It should be noted that the majority

of these measurements (not including the background sites of Pt. Arguello and San Nicolas Island) were made during pollution episode conditions and, therefore, will be in the upper range of the concentrations to which the populations at these sites are exposed.

The BaP concentrations ranged from not quantifiable at the background sites of Pt. Arguello and San Nicolas Island (the limit of detection is estimated to have been $\leq 10 \text{ pg m}^{-3}$) to a high at Mammoth Lakes during the wood-burning season of $\sim 12 \text{ ng m}^{-3}$.

Table 2. Ambient Benzo[a]pyrene Concentrations for Locations in Contra Costa County, CA (From Flessel et al., 1984)

| Location Site and Dates ^a | | | Benzo[a]pyrene (ng m ⁻³) |
|--------------------------------------|-------------|-------|--------------------------------------|
| Richmond | 8/6/81 | Day | 0.1 |
| | 8/6-7/81 | Night | 0.1 |
| | 8/7/81 | Day | 0.1 |
| Martinez | 8/6/81 | Day | 0.1 |
| | 8/6-7/81 | Night | 0.1 |
| | 8/7/81 | Day | 0.1 |
| Concord | 8/6/81 | Day | 0.1 |
| | 8/6-7/81 | Night | 0.1 |
| | 8/7/81 | Day | 0.1 |
| Pittsburg | 8/6/81 | Day | 0.1 |
| | 8/6-7/81 | Night | 0.1 |
| | 8/7/81 | Day | 0.1 |
| Richmond | 10/20-21/81 | Night | 0.1 |
| | 10/21/81 | Day | 0.2 |
| | 10/21-22/81 | Night | 0.1 |
| Martinez | 10/20-21/81 | Night | 0.8 |
| | 10/21/81 | Day | 0.4 |
| | 10/21-22/81 | Night | 0.1 |
| Concord | 10/20-21/81 | Night | 1.1 |
| | 10/21/81 | Day | 0.4 |
| | 10/21-22/81 | Night | 1.5 |
| Pittsburg | 10/20-21/81 | Night | 0.2 |
| | 10/21/81 | Day | 0.2 |
| | 10/21-22/81 | Night | 0.2 |
| Richmond | 1/13-14/82 | Night | 2.0 |
| | 1/14/82 | Day | 0.8 |
| | 1/14-15/82 | Night | 2.6 |
| Martinez | 1/13-14/82 | Night | 0.4 |
| | 1/14/82 | Day | 0.2 |
| | 1/14-15/82 | Night | 1.5 |

Table 2 (continued) - 2

| Location Site and Dates ^a | | | Benzo[a]pyrene (ng m ⁻³) |
|--------------------------------------|------------|-------|--------------------------------------|
| Concord | 1/13-14/82 | Night | 2.6 |
| | 1/14/82 | Day | 0.6 |
| | 1/14-15/82 | Night | 2.6 |
| Pittsburg | 1/13-14/82 | Night | 1.3 |
| | 1/14/82 | Day | 0.5 |
| | 1/14-15/82 | Night | 1.1 |

^aFor complete details of sampling and pollution episode conditions see Flessel et al. (1984).

Table 3. Ambient Benzo[a]pyrene and Benzo[e]pyrene Concentrations for Claremont and Torrance, CA (From Winer et al., 1987)

| Location Site and Dates ^a | | | ng m ⁻³ | |
|--------------------------------------|------------|--------------|--------------------|-----------------|
| | | | Benzo[a]-pyrene | Benzo[e]-pyrene |
| Claremont | 9/14/85 | 0600-1200 hr | 0.09 | 0.28 |
| Claremont | 9/14/85 | 1200-1800 hr | 0.04 | 0.13 |
| Claremont | 9/14/85 | 1800-2400 hr | 0.14 | 0.36 |
| Claremont | 9/15/85 | 0000-0600 hr | 0.03 | 0.13 |
| Torrance | 2/24-25/86 | Night | 1.6 | 2.1 |
| Torrance | 2/25/86 | Day | 0.6 | 2.1 |

^aSee Winer et al. (1987) for full details of pollution episodes sampled.

Table 4. Ambient Benzo[a]pyrene and Benzo[e]pyrene Concentrations for Locations Throughout California (From Atkinson et al., 1988)

| Location Site and Dates ^a | | | ng m ⁻³ b | |
|--------------------------------------|-----------|-------|----------------------|---------------------|
| | | | Benzo[a]- pyrene | Benzo[e]- pyrene |
| Glendora | Sample #1 | Day | 0.26 | 0.62 |
| 8/13/86 | | | | |
| Glendora | Sample #2 | Night | 0.62 | 1.54 |
| 8/13-14/86 | | | | |
| Glendora | Sample #3 | Day | 0.18 | 0.41 |
| 8/15, 16, 17, 18/86 | | | | |
| Glendora | Sample #4 | Night | 0.18 | 0.65 |
| 8/15-16, 16-17, 17-18, 18-19/86 | | | | |
| Glendora | Sample #5 | Day | 0.23 | 0.83 |
| 8/20/86 | | | | |
| Glendora | Sample #6 | Night | 0.32 | 0.95 |
| 8/20-21/86 | | | | |
| Yuba City | Sample #1 | Day | 0.13 | 0.35 |
| 10/16, 18, 20/86 | | | | |
| Yuba City | Sample #2 | Day | 0.32 | 0.66 |
| 10/17, 23/86 | | | | |
| Yuba City | Sample #3 | Night | 0.22 | 0.34 |
| 10/16-17, 18-19, 20-21, 23-24/86 | | | | |
| Concord | Sample #1 | Day | 1.77 | 1.91 |
| 12/8, 9/86; 1/19/87 | | | | |
| Concord | Sample #2 | Day | 3.23 | 2.77 |
| 1/18, 21, 22/87 | | | | |
| Concord | Sample #3 | Night | 6.15 | 4.22 |
| 12/6-7, 7-8, 8-9/86 | | | | |
| Concord | Sample #4 | Night | 8.15 | 5.76 |
| 1/17-18, 18-19, 21-22/87 | | | | |
| Concord | Sample #5 | Night | 1.93 | 1.52 |
| 12/10-11/86; 1/14-15/87 | | | | |

Table 4 (continued) - 2

| Location Site and Dates ^a | ng m ⁻³ b | |
|---|----------------------|-----------------|
| | Benzo[a]-pyrene | Benzo[e]-pyrene |
| Mammoth Lakes Sample #1 Day 2/14, 16, 17, 21, 22, 26, 28/87 | 3.56 | 2.57 |
| Mammoth Lakes Sample #2 Night 2/16-17, 17-18, 20-21, 27-28; 2/28-3/1/87 | 12.49 | 8.00 |
| Mammoth Lakes Sample #3 Night 2/14-15, 15-16, 21-22, 22-23, 25-26/87 | 3.14 | 2.05 |
| Oildale Sample #1 Day 3/30, 31/87; 4/1, 2, 7, 8, 9, 10/87 | 0.42 | 0.44 |
| Oildale Sample #2 Night 3/29-30/87; 4/9-10, 10-11/87 | 0.17 | 0.25 |
| Oildale Sample #3 Night 3/31-4/1/87; 4/1-2, 7-8, 8-9/87 | 0.88 | 0.98 |
| Reseda Sample #1 Day 5/28, 29, 30, 31/87; 6/1, 2, 14, 15/87 | 0.47 | 0.71 |
| Reseda Sample #2 Night 5/27-28, 28-29, 29-30, 30-31, 5/31-6/1; 6/1-2, 2-3, 13-14, 14-15/87 | 0.13 | 0.28 |
| Pt. Arguello Sample #1 Day 7/4, 5, 6, 7, 8, 9, 10, 11, 12/87 | c | 0.005 |
| Pt. Arguello Sample #2 Night 7/4-5, 5-6, 6-7, 7-8, 8-9, 9-10, 10-11, 11-12/87 | c | 0.008 |
| San Nicolas Island Composite 6/19, 24, 25; 7/13, 14, 15; 8/27, 28, 29; 9/2, 3/87; 6/19-20, 24-25, 25-26/87; 7/13-14, 14-15, 15-16/87; 8/27-28, 28-29, 29-30/87; 9/3-4/87 | c | 0.005 |

^aSee Atkinson et al. (1988) for full details of compositing.

^bAverage of replicate GC/MS injections.

^cAmount present too low to quantify.

F. References

- Arey, J., Zielinska, B., Atkinson, R., and Winer A. M. (1987): Polycyclic aromatic hydrocarbon and nitroarene concentrations in ambient air during a winter-time high-NO_x episode in the Los Angeles basin. *Atmos. Environ.* 21, 1437-1444.
- Arey, J., Zielinska, B., Atkinson, R., and Winer, A. M. (1988): Formation of nitroarenes during ambient high-volume sampling. *Environ. Sci. Technol.*, 22, 457-462.
- Atkinson, R., Arey, J., Winer, A. M., Zielinska, B., Dinoff, T. M., Harger, W. P. and McElroy, P. A. (1988): A Survey of Ambient Concentrations of Selected Polycyclic Aromatic Hydrocarbons (PAH) at Various Locations in California. Final Report, California Air Resources Board Contract No. A5-185-32, May.
- Behymer, T. D. and Hites, R. A. (1985): Photolysis of polycyclic aromatic hydrocarbons adsorbed on simulated atmospheric particulates. *Environ. Sci. Technol.*, 19, 1004-1006.
- Behymer, T. D. and Hites, R. A. (1988): Photolysis of polycyclic aromatic hydrocarbons adsorbed on fly ash. *Environ. Sci. Technol.*, 22, 1311-1319.
- Bidleman, T. F. (1988): Atmospheric processes. *Environ. Sci. Technol.*, 22, 361-367.
- Blau, L. and Güsten, H. (1981): Quantum yields of the photodecomposition of polynuclear aromatic hydrocarbons adsorbed on silica gel. In: Aromatic Hydrocarbons, M. Cooke, A. J. Dennis and G. L. Fisher (Eds.), Battelle Press, Columbus, OH, pp. 133-144.
- Bockhorn, H., Fetting, F., Wannemacher, G. and Wenz, H. W. (1982): Optical studies of soot particle growth in hydrocarbon oxygen flames. 19th Int. Symp. on Combustion, 1982; The Combustion Institute, Pittsburgh, PA, pp. 1413-1420.
- Brorström, E., Grennfelt, P. and Lindskog, A. (1983): The effect of nitrogen dioxide and ozone on the decomposition of particle-associated polycyclic aromatic hydrocarbons during sampling from the atmosphere. *Atmos. Environ.*, 17, 601-605.
- Brorström-Lundén, E. and Lindskog, A. (1985): Degradation of polycyclic aromatic hydrocarbons during simulated stack gas sampling. *Environ. Sci. Technol.*, 19, 313-316.
- Butler, J. D. and Crossley, P. (1981): Reactivity of polycyclic aromatic hydrocarbons adsorbed on soot particles. *Atmos. Environ.*, 15, 91-94.

- Coutant, R. W., Brown, L., Chuang, J. C., Riggan, R. M. and Lewis, R. G. (1988): Phase distribution and artifact formation in ambient air sampling for polynuclear aromatic hydrocarbons. *Atmos. Environ.*, 22, 403-409.
- Eisenreich, S. J., Looney B. B. and Thornton, J. D. (1981): Airborne organic contamination in the Great Lakes ecosystem. *Environ. Sci. Technol.*, 15, 30-38.
- Flessel, P., Guirguis, G., Cheng, J., Chang, K., Hahn, E., Chan, R., Ondo, J., Fenske, R. Twiss, S., Vance, W. and Wesolowski, J. (1984): Monitoring of Mutagens and Carcinogens in Community Air. Final Report, California Air Resources Board Contract No. A1-029-32, May.
- Gibson, T. L. (1982): Nitroderivatives of polynuclear aromatic hydrocarbons in airborne and source particulate matter. *Atmos. Environ.*, 16, 2037-2040.
- Gibson, T. L. (1983): Sources of direct-acting nitroarene mutagens in airborne particulate matter. *Mutat. Res.*, 122, 115-121.
- Graedel, T. E., and Weschler, C. J. (1981): Chemistry within aqueous atmospheric aerosols and raindrops. *J. Geophys. Res.*, 19, 505-539.
- Grosjean, D., Fung, K. and Harrison, J. (1983): Interactions of polycyclic aromatic hydrocarbons with atmospheric pollutants. *Environ. Sci. Technol.*, 17, 673-679.
- Güsten, H. (1986): Photocatalytic degradation of atmospheric pollutants on the surface of metal oxides. In: Chemistry of Multiphase Atmospheric Systems, W. Jaeschke (Ed.), Springer-Verlag, Berlin, pp. 567-592.
- IARC Monographs (1983): IARC Monographs on the Evaluation of the Carcinogenic Risk of Chemicals to Humans. Polynuclear Aromatic Compounds, Part 1, Chemical, Environmental and Experimental Data, Vol. 32, International Agency for Research on Cancer, France, pp. 211-224.
- Jäger, J. and Hanus, V. (1980): Reaction of solid carrier-adsorbed polycyclic aromatic hydrocarbons with gaseous low-concentrated nitrogen dioxide. *J. Hyg. Epidemio. Microbio. Immunol.*, 24, 1-12.
- Kamens, R., Bell, D., Dietrich, A., Perry, J., Goodman, R., Claxton, L. and Tejada, S. (1985): Mutagenic transformations of dilute wood smoke systems in the presence of ozone and nitrogen dioxide. Analysis of selected high-pressure liquid chromatography fractions from wood smoke particle extracts. *Environ. Sci. Technol.*, 19, 63-69.
- Kamens, R. M., Fulcher, J. N. and Zhishi, G. (1986): Effects of temperature on wood soot PAH decay in atmospheres with sunlight and low NO_x. *Atmos. Environ.*, 20, 1579-1587.

- Kamens, R. M., Zhishi, G., Fulcher, J. N. and Bell, D. A. (1988): Influence of humidity, sunlight, and temperature on the daytime decay of polyaromatic hydrocarbons on atmospheric soot particles. *Environ. Sci. Technol.*, 22, 103-108.
- Katz, M., Chan, C., Tosine, H. and Sakuma, T. (1979): Relative rates of photochemical and biological (in vitro) oxidation of polynuclear aromatic hydrocarbons. In: *Polynuclear Aromatic Hydrocarbons*, P. W. Jones and P. Leber (Eds.), Ann Arbor Science Publishers, Ann Arbor, MI, pp. 171-189.
- Kittelson, D. B., Du, C.-J. and Zweidinger, R. B. (1985): Measurements of polycyclic aromatic compounds in the cylinders of an operating diesel engine. EPA-600/D-85/012, January.
- Korfmacher, W. A., Natusch, D. F. S., Taylor, D. R., Mamantov, G. and Wehry, E. L. (1980): Oxidative transformations of polycyclic aromatic hydrocarbons adsorbed on coal fly ash. *Science*, 207, 763-765.
- Leuenberger, C., Ligocki, M. P., and Pankow, J. F. (1985): Trace organic compounds in rain. 4. Identities, concentrations and scavenging mechanisms for phenols in urban air and rain. *Environ. Sci. Technol.* 19, 1053-1058.
- Ligocki, M. P., Leuenberger, C., and Pankow, J. F. (1985): Trace organic compounds in rain. III. Particle scavenging of neutral organic compounds. *Atmos. Environ.* 19, 1619-1626.
- Lindskog, A., Brorström-Lundén, E. and Sjödin, Å. (1985): Transformation of reactive PAH on particles by exposure to oxidized nitrogen compounds and ozone. *Environ. Internat.*, 11, 125-130.
- Nielsen, T. (1984): Reactivity of polycyclic aromatic hydrocarbons toward nitrating species. *Environ. Sci. Technol.*, 18, 157-163.
- Nielsen, T. (1988): The decay of benzo[a]pyrene and cyclopenteno[cd]-pyrene in the atmosphere. *Atmos. Environ.*, 22, 2249-2254.
- Nikolaou, K., Masclet, P. and Mouvier, G. (1984): Sources and chemical reactivity of polynuclear aromatic hydrocarbons in the atmosphere - a critical review. *Sci. Total Environ.*, 32, 103-132.
- Paputa-Peck, M. C., Marano, R. S., Schuetzle, D., Riley, T. L., Hampton, C. V., Prater, T. J., Skewes, L. M., Jensen, T. E., Ruehle, P. H., Bosch, L. C. and Duncan, W. P. (1983): Determination of nitrated polynuclear aromatic hydrocarbons in particulate extracts by capillary column gas chromatography with nitrogen selective detection. *Anal. Chem.*, 55, 1946-1954.
- Peters, J. and Seifert, B. (1980): Losses of benzo(a)pyrene under the conditions of high-volume sampling. *Atmos. Environ.*, 14, 117-119.

- Pierce, R. C. and Katz, M. (1975): Dependency of polynuclear aromatic hydrocarbon content on size distribution of atmospheric aerosols. *Environ. Sci. Technol.*, 9, 347-353.
- Pitts, J. N., Jr., Van Cauwenberghe, K. A., Grosjean, D., Schmid, J. P., Fitz, D. R., Belser, W. L., Jr., Knudson, G. B. and Hynds, P. M. (1978): Atmospheric reactions of polycyclic aromatic hydrocarbons: facile formation of mutagenic nitro derivatives. *Science*, 202, 515-519.
- Pitts, J. N., Jr., Lokensgard, D. M., Ripley, P. S., Van Cauwenberghe, K. A., Van Vaeck, L., Shaffer, S. D., Thill, A. J. and Belser, W. L., Jr. (1980): "Atmospheric" epoxidation of benzo(a)pyrene by ozone: formation of the metabolite benzo(a)pyrene-4,5-oxide. *Science*, 210, 1347-1349.
- Pitts, J. N., Jr., Sweetman, J. A., Zielinska, B., Atkinson, R., Winer, A. M. and Harger, W. P. (1985): Formation of nitroarenes from the reaction of polycyclic aromatic hydrocarbons with dinitrogen pentaoxide. *Environ. Sci. Technol.*, 19, 1115-1121.
- Pitts, J. N., Jr., Paur, H.-R., Zielinska, B., Arey, J., Winer, A. M., Ramdahl, T. and Mejia, V. (1986): Factors influencing the reactivity of polycyclic aromatic hydrocarbons adsorbed on filters and ambient POM with ozone. *Chemosphere*, 15, 675-685.
- Prado, G., Garo, A., Ko, A. and Sarofim, A. (1985): Polycyclic aromatic hydrocarbons: formation and destruction in a laminar diffusion flame. 20th Int. Symp. on Combustion 1984; The Combustion Institute, Pittsburgh, PA, pp. 989-996.
- Ramdahl, T., Bjorseth, A., Lokensgard, D. M. and Pitts, J. N., Jr. (1984): Nitration of polycyclic aromatic hydrocarbons adsorbed to different carriers in a fluidized bed reactor. *Chemosphere*, 13, 527-534.
- Schuetzle, D. and Frazier, J. A. (1986): Factors influencing the emission of vapor and particulate phase components from diesel engines. In: Carcinogenic and Mutagenic Effects of Diesel Engine Exhaust, N. Ishinishi, A. Koizumi, R. O. McClellan and W. Stöber (Eds.), Elsevier Science Publishers B. V., pp. 41-63.
- Toqan, M., Farmayan, W. R., Beér, J. M., Howard, J. B. and Teare, J. D. (1985): PAH and soot formation in fuel-rich turbulent coal liquid and natural gas diffusion flames. 20th Int. Symp. on Combustion, 1984, The Combustion Institute, Pittsburgh, PA, pp. 1075-1081.
- Van Vaeck, L. and Van Cauwenberghe, K. (1984): Conversion of polycyclic aromatic hydrocarbons on diesel particulate matter upon exposure to ppm levels of ozone. *Atmos. Environ.*, 18, 323-328.
- Valerio, F., Antolini, E. and Lazzarotto, A. (1987): A model to evaluate half-lives of PAHs naturally occurring on airborne particulate. *Intern. J. Environ. Anal. Chem.*, 28, 185-196.

- Winer, A. M., Atkinson, R., Arey, J., Biermann, H. W., Harger, W. P., Tuazon, E. C. and Zielinska, B. (1987): The Role of Nitrogenous Pollutants in the Formation of Atmospheric Mutagens and Acid Deposition. Final Report, California Air Resources Board Contract No. A4-081-32, March.
- Wise, S. A., Chesler, S. N., Hilpert, L. R., May, W. E., Rebbert, R. E., Vogt, C. R., Nishioka, M. G., Austin, A., Lewtas, J. (1985): Quantification of polycyclic aromatic hydrocarbons and nitro-substituted polycyclic aromatic hydrocarbons and mutagenicity testing for the characterization of ambient air particulate matter. Environ. Int., 11, 147-160.
- Yamasaki, H., Kuwata, K. and Kuge, Y. (1984): Determination of vapor pressure of polycyclic aromatic hydrocarbons in the supercooled liquid phase and their adsorption on airborne particulate matter. J. Chem. Soc. Japan, 8, 1324-1329.
- Yokley, R. A., Garrison, A. A., Mamantov, G. and Wehry, E. L. (1985): The effect of nitrogen dioxide on the photochemical and nonphotochemical degradation of pyrene and benzo[a]pyrene adsorbed on coal fly ash. Chemosphere, 14, 1771-1778.
- Yokley, R. A., Garrison, A. A., Wehry, E. L. and Mamantov, G. (1986): Photochemical transformation of pyrene and benzo[a]pyrene vapor-deposited on eight coal stack ashes. Environ. Sci. Technol., 20, 86-90.