FORMATION AND FATE OF TOXIC CHEMICALS IN CALIFORNIA'S ATMOSPHERE

Final Report

Contract No. A2-115-32

California Air Resources Board

July 1984

Principal Investigator

James N. Pitts, Jr.

Co-Principal Investigators

Roger Atkinson
Arthur M. Winer

Research Staff

Heinz W. Biermann
William P. L. Carter
Hélène Mac Leod
Ernest C. Tuazon

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

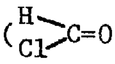
ABSTRACT

Although the atmospheric chemistry of NO_x/hydrocarbon systems involved in photochemical smog formation is becoming well understood, little is known today about the environmental fates of airborne toxic organic chemicals. Relevant chemical questions include: What are their ambient levels? How fast do they degrade in "clean" vs polluted ambient air? What are their reaction products?

Since the study of all volatile toxic organics would be an overwhelming experimental task and prohibitively expensive, we have initiated an investigation of representative compounds relevant to California's polluted ambient and occupational atmospheres. The results of these experimental studies will contribute to a data base that will be the foundation for a sound predictive capability to assess the potential risk of many toxic organic chemicals currently in use in California. This new data base could also be used to predict the atmospheric lifetimes and fates of new compounds being synthesized for industrial and agricultural use.

Compounds studied include 1,3-dichloropropene (widely used as an agricultural insecticide fumigant), vinyl chloride (a carcinogen emitted from chemical manufacturing plants as well as waste chemical sites) and tri- and tetrachloroethylene (widely used solvents which are suspected carcinogens). Experiments were carried out in the SAPRC 5800-ℓ evacuable chamber-solar simulator facility using both *in situ* Fourier transform infrared (FT-IR) spectroscopy and UV/visible differential optical absorption spectroscopy (DOAS) to identify and quantify the reaction products.

The atmospheric half-lives of the *cis*- and *trans*-1,3-dichloropropene isomers toward attack by OH radicals in simulated moderately polluted air were found to be 7 hr and 12 hr, respectively, while the half-lives for reaction with O_3 were determined to be approximately 2 weeks and 7 weeks, respectively. Major products formed from the reaction of OH radicals with 1,3-dichloropropene included formyl chloride ($HCCl$) and chloroacetaldehyde ($ClCH_2CHO$).

With respect to the chloroethylenes reaction of vinyl chloride with OH radicals gave an ~100% yield of formyl chloride ( $\genfrac{}{}{0pt}{}{H}{Cl}\!>\!C{=}O$), a toxic

photolabile species while trichloroethylene formed both phosgene ($COCl_2$) and formyl chloride in each case with ~20-25% yield each. An ~50-55% yield of phosgene was formed from OH attack on tetrachloroethylene.

A major study was completed of the atmospheric chemistry of three aromatic hydrocarbons, toluene and o- and m-xylene, which are present in substantial concentrations in unleaded gasoline. Products of hydroxyl radical-initiated, ring opening photooxidation included the α-dicarbonyl species glyoxal and methylglyoxal. However their yields were much lower than those currently used in chemical computer models describing the atmospheric degradation of aromatic hydrocarbons. Indeed, for toluene the identified reaction pathways following OH attack account for only ~50% of the overall reaction. Clearly, in order to improve the validity of widely used kinetic-computer models of photochemical air pollution, more extensive research needs to be carried out on the products and mechanisms of such OH-aromatic hydrocarbon reactions.

In another study, alkyl nitrate ($RONO_2$) yields were determined for a series of NO_x-air photooxidations of branched and cyclic alkanes. The latter are major constituents of diesel, gasoline and aviation fuels and the nitrates are important reaction products. Alkanes studied were: neopentane, 2,3-dimethylbutane, 2,2-dimethylbutane, 3-methylpentane and cyclohexane. Since the reaction

$$RO_2 + NO \xrightarrow{M} RONO_2$$

is a removal process for both NO_x and radicals, it has a marked effect in decreasing the photochemical reactivity of these longer chain alkanes. The data obtained in this work, together with our previous studies, now allow a-priori predictions of the significance of this reaction for the alkanes emitted into the atmosphere from anthropogenic sources.

TABLE OF CONTENTS

TABLE OF CONTENTS

ACKNOWLEDGMENTS

Stimulating discussion and valuable exchanges of technical information, for which we express our appreciation, took place at various times during this program with Drs. John R. Holmes and Jack K. Suder, members of the California Air Resources Board research staff. We gratefully acknowledge Ms. Sara M. Aschmann and Mr. William D. Long for assistance in carrying out this research, and Ms. Christy LaClaire for typing this report.

This report was submitted in fulfillment of Contract No. A2-115-32 by the Statewide Air Pollution Center, University of California, Riverside, under the partial sponsorship of the California Air Resources Board. Work was completed as of July 19, 1984.

LIST OF FIGURES

LIST OF FIGURES

LIST OF TABLES

LIST OF TABLES

I. PROJECT SUMMARY

A. Introduction and Statement of the Problem

1. The Lifetimes and Fates of Toxic Chlorinated Olefins in the Atmosphere

While we now have a reasonable understanding of the chemistry of hydrocarbons associated with the formation of photochemical air pollution, little is known about the mechanisms, products and, in many cases, lifetimes associated with the atmospheric degradation pathways of many other classes of organics containing O, S, N or halogen atoms (Atkinson et al. 1979). These compounds are presently emitted into the atmosphere through manufacturing processes, fuel usage, and solvent evaporation, as well as from chemical waste sites.

Since many of these organics are, or may be, toxic, there is a growing concern in the U.S., and in California in particular, over the health effects of such chemicals. However, in order to develop accurate risk/assessment evaluations for these volatile organics, a much more detailed knowledge of their atmospheric lifetimes and fates is required than presently exists.

The study of all such organics would be a monumental and prohibitively expensive experimental task; therefore we decided to study carefully selected representative members of the various classes of organic compounds relevant to the needs of California. These include the carcinogen vinyl chloride and certain widely used halogenated solvents, as well as the ubiquitous insecticide fumigant 1,3-dichloropropene. The experimental results derived from these chamber studies will provide a data base from which the lifetimes, products and mechanisms for other homologues or analogues can be estimated with reasonable reliability, thus minimizing time-consuming and expensive experimental research.

2. Reaction Products and Rates of Formation for Representative Aromatic and Aliphatic Hydrocarbons in Fuels for Gasoline and Diesel Engines

Today the mechanisms of formation of O_3, PAN and certain other secondary pollutants (i.e., formaldehyde, HCHO) are reasonably well understood for approximately a dozen paraffinic, olefinic and aromatic hydrocarbons. However, there are two specific areas that are important in the overall chemistry of these simple HC/NO_x systems for which additional experimental data are required. These are (a) the mechanisms and products of the photooxidations of aromatic hydrocarbon-NO_x-air systems and (b) the efficiencies of formation of alkyl nitrates from NO_x-air photooxidations of the higher alkanes. These two research areas are especially relevant to California's air pollution problems since aromatic hydrocarbons constitute a large fraction of unleaded gasoline, and the higher alkanes ($\geq C_6$) are major constituents of diesel fuels.

During our previous ARB program (Contract No. A1-030-32) we initiated studies of both of these systems, and our results proved to be both fundamentally interesting and useful to atmospheric scientists employing models of photochemical air pollution for development of control strategies. In the present program we completed our studies in these two areas and our detailed results are presented in this report.

B. Objectives

The specific objectives of this program were:

- To investigate the atmospheric chemistry of the two 1,3-dichloropropene isomers. These are widely used as agricultural insecticides in California under a variety of trade names.
- To investigate the atmospheric chemistry of three toxic chloroethylenes, vinyl chloride (an industrially used carcinogen) and tri- and tetrachloroethylene (widely used solvents which are suspected carcinogens).
- To determine the oxygenated products formed from the NO_x-air photooxidations of the aromatic hydrocarbons toluene and m- and p-xylene, important constituents of unleaded gasoline.
- To determine the yields of alkyl nitrates formed directly from the reaction of alkyl peroxy radicals with NO at room temperature and atmospheric pressure, a process previously shown to be important for the long chain alkane constituents of gasoline and diesel fuels.

C. Approach

The research carried out in this program was made possible by the unique experimental facilities available at the Statewide Air Pollution Research Center (SAPRC), funded by previous CARB programs as well as by the National Science Foundation, U. S. Environmental Protection Agency and other agencies. In particular, for the majority of these investigations the SAPRC 5800-ℓ evacuable thermostatted environmental chamber was used in conjunction with our 25 KW arc solar simulator. Rate constant determinations and monitoring of the disappearance of reactants and the appearance of products were carried out by in situ long pathlength Fourier transform infrared (FT-IR) spectroscopy or by use of an in situ differential optical absorption spectrometer (DOAS) in the UV-visible spectral region (or both). In addition to these spectroscopic techniques, appropriate gas chromatograph methods were employed as needed.

Detailed information concerning these and other experimental methods used are provided in Sections II-V of our report.

D. Summary of Results and Conclusions

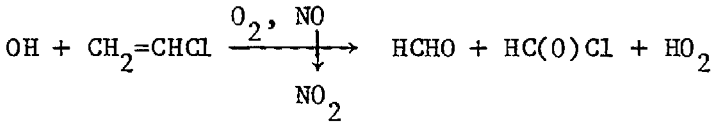
The principal findings obtained in this investigation and the conclusions which may be drawn from them are as follows:

- The rate constants for the reactions of OH radicals with cis- and trans-1,3-dichloropropene were determined to be 0.77 and 1.31 x 10^{-11} cm^3 $molecule^{-1}$ sec^{-1}, respectively. The analogous rate constants for reaction of these isomers with ozone were determined to be (1.5 ± 0.5) and (6.7 ± 0.8) x 10^{-19} cm^3 $molecule^{-1}$ sec^{-1}, respectively. Based on appropriately chosen ambient concentrations for O_3 and OH radicals the corresponding atmospheric half-lives with respect to reaction with ozone are 12 days and 52 days and with respect to reaction with OH radicals 7 hr and 12 hr for the trans- and cis-forms of 1,3-dichloropropene, respectively.

These experiments also indicated that the only significant loss process for 1,2-dichloropropane in the atmosphere would be reaction with OH radicals, for which a half-life of $\gtrsim$13 days is estimated for a 24-hr average OH radical concentration of 1 x 10^6 cm^{-3}. This result is of interest since 1,2-dichloropropane, along with the cis- and trans-1,3-dichloropropenes, is an important component of the fumigant formulations D-D and Telone.

In evaluating the possible harmful effects of 1,3-dichloropropene, it would be prudent as well to consider the potential health risks associated with the products of the 1,3-dichloropropene reaction with OH radicals, namely formyl chloride (HCCl) and chloroacetaldehyde ($ClCH_2CHO$). Whereas formyl chloride is known to eventually decompose and hydrolyze to CO, HCl, and HCOOH, the other toxic product chloroacetyladehyde may actually persist appreciably longer in the environment. Of course the levels of these products may be low enough so as to not constitute a threat, except possibly in specific occupational settings.

Our observed unit yield of formyl chloride from vinyl chloride implies a corresponding unit yield of formaldehyde, and shows that the reaction of OH radicals with vinyl chloride proceeds via essentially 100% cleavage of the double bond:



$$OH + CH_2{=}CHCl \xrightarrow[NO_2]{O_2,\ NO} HCHO + HC(O)Cl + HO_2$$

However, for trichloroethylene, the yields of formyl chloride and phosgene, though essentially identical, are only ~20-25%. Hence it is evident that the reaction of OH radicals with trichloroethylene leads, ~75-80% of the time, to products other than these cleavage products observed. An analogous situation occurs in the case of tetrachloroethylene, where the observed ~53% yield of $COCl_2$ shows that the above discussed reaction scheme leaving to cleavage of the double bond occurs only ~25% of the time, with other unidentified products being formed in the majority of the reaction.

- The yields of the ring cleavage products, the α-dicarbonyl compounds glyoxal and methylglyoxal, from attack of OH radicals on the aromatic hydrocarbons toluene and m- and p-xylene, were determined at room temperature and atmospheric pressure. Our yields of these α-dicarbonyls are much lower than those which have been used in previous chemical computer models for the atmospheric degradation of these aromatic hydrocarbons. In fact for toluene the identified reaction pathways subsequent to the initial OH radical reaction account for only ~50% of the overall reaction. Clearly the products and mechanisms of a major portion of the OH-aromatic reactions under atmospheric conditions are presently not identified. This has major implications for urban airshed models currently being used to develop control strategies for photochemical air pollution.

- The yields of alkyl nitrates were determined for the NO_x-air photooxidations of neopentane, cyclohexane, 2-methylbutane, 2-methylpentane and 3-methylpentane. Specifically, we have determined the formation of alkyl nitrates from the reactions of NO with alkyl peroxy radicals generated from these cyclic or branched alkanes at 298 ± 2 K and 735 torr total pressure. In addition, rate constants for the reaction of OH radicals with several of the alkyl nitrates formed in these systems were also determined.

Since the reaction

$$RO_2 + NO \xrightarrow{M} RONO_2$$

is a removal process for both NO_x and radicals, it has a marked effect in decreasing the photochemical reactivity of these longer chain alkanes. The data obtained in this work, together with our previous studies, now allow approximate a-priori predictions of the significance of this reaction for the alkanes emitted into the atmosphere from anthropogenic uses.

E. Recommendations for Future Research

- It is important to investigate the atmospheric transformations and loss processes of other "model" organic compounds representative of various classes of airborne toxic organics. These model compounds should be chosen to contain functional groups or chemical structures which are found in a wide range of airborne volatile industrial and agricultural chemicals.
- Specific values are needed for the rate constants for the reactions of these model compounds with ozone and with OH and NO_3 radicals so that their atmospheric lifetimes can be calculated. In addition, the products resulting from such reactions must be characterized.
- These combined kinetic and product data for appropriate model compounds should be used to develop a-priori predictive techniques for assessing, in a time- and cost-effective manner, the atmospheric lifetimes and fates of many airborne toxic chemicals currently in use.

II. THE ATMOSPHERIC CHEMISTRY OF THE AGRICULTURALLY IMPORTANT INSECTICIDE 1,3-DICHLOROPROPENE

A. Introduction

One of the organo-chlorine compounds that has increased in importance in recent years as an agricultural chemical is 1,3-dichloropropene (cis- and trans-$ClCH_2CH=CHCl$). This chemical is an insecticide fumigant which is effective against soil nematodes. Commercial products used for such a purpose are the "D-D" mixture (Shell Development Co.) and "Vidden D" (Dow Chemical Co.) which are produced by high-temperature chlorination of propene, and consist of $\gtrsim$50% of the two isomers of 1,3-dichloropropene plus 1,2-dichloropropane ($CH_3CHClCH_2Cl$) and related C_3 compounds (Worthing 1979). Other formulations include those by Dow Chemical Co. under the trademarks "Telone" (78.5% 1,3-dichloropropene, 20.5% 1,2-dichloropropane and related compounds), "Telone II" (92% 1,3-dichloropropene), and "Telone C17" (76.3% 1,3-dichloropropene, 17.1% chloropicrin) (Caswell et al. 1981, Worthing 1979).

The widespread use of this compound is illustrated by data from the California State Department of Food and Agriculture which shows that in California alone the use of 1,3-dichloropropene in various formulations increased from 5.5 million lb in 1978 to 16.4 million lb of active ingredient in 1981, although a drop to 12.3 million lb was recorded for 1982 (Fleck 1983). Due to its high volatility, and the methods involved in its use as a fumigant, it is certain that a significant proportion of 1,3-dichloropropene finds its way into the atmosphere during application.

It is generally recognized that under atmospheric conditions the major loss processes for organics are photolysis and reaction with ozone (O_3), the hydroxyl (OH) radical, and the nitrate (NO_3) radical (Hendry and Kenley 1979, Herron et al. 1979, Atkinson et al. 1979, 1984b). For the 1,3-dichloropropene isomers, which do not absorb actinic (i.e., wavelengths $\gtrsim$290 nm) radiation (see, for example, UV Atlas of Organic Compounds, New York, Plenum Press, 1967, Vol. III, pp. A1/7-A1/8), the kinetic data available for other alkenes and haloalkenes (Hendry and Kenley 1979, Atkinson et al. 1979, 1984b, Pitts 1983, Atkinson and Lloyd 1984) indicate that the reactions with O_3 and OH radicals are expected to be the dominant atmospheric loss processes. Thus, in this study rate constants for the reactions of both trans- and cis-1,3-dichloropropene with O_3 and the OH radical were measured and investigations of the products formed were carried out. The extent of these reactions for 1,2-dichloropropane was also examined since, as noted above, this compound is an important component of the more widely used 1,3-dichloropropene formulations.

To carry out these studies we employed an environmental chamber with long-path Fourier-transform infrared (FT-IR) spectroscopic analyses of reactants and products, at part-per-million (ppm) concentrations of reactants in air. The rate constants obtained, along with literature values for other chloroalkenes, yield a data set which enables the effects of chlorine atom substitution on the reactivity, and hence lifetimes, of these compounds toward O_3 and the OH radical to be assessed.

B. Experimental

1. Kinetic Experiments

The technique for the determination of ozone reaction rate constants was based on observing the increased rate of ozone decay in the presence of a known excess of a reactive compound, and has been described in detail previously (Atkinson et al. 1981a, 1983b). In the presence of such a reactant, the processes removing O_3 are:

$$O_3 + \text{wall} \rightarrow \text{loss of } O_3 \tag{1}$$

$$O_3 + \text{reactant} \rightarrow \text{products} \tag{2}$$

and hence

$$\frac{-d[O_3]}{dt} = (k_1 + k_2[\text{reactant}])[O_3] \tag{I}$$

where k_1 and k_2 are the rate constants for reactions (1) and (2). With the reactant concentration being in large excess over the initial O_3 concentration ($[\text{reactant}]/[O_3]_{\text{initial}} \gtrsim 10$), the reactant concentration remains essentially constant throughout the reaction, and equation (I) may be rearranged to yield:

$$\frac{-d\ln[O_3]}{dt} = k_1 + k_2[\text{reactant}] \qquad \text{(II)}$$

Thus, from the dependence of the ozone decay rate, $-d\ln[O_3]/dt$, on the reactant concentration, and with a knowledge of the background ozone decay rate k_1, the rate constant k_2 may be readily obtained.

As described previously (Atkinson et al. 1981a, 1983b), reactions were carried out in a ~160-ℓ volume Teflon bag, constructed out of a 2-mil thick, 180 x 140-cm FEP Teflon sheet, heat-sealed around the edges and fitted with Teflon injection and sampling ports at each end of the bag. The reaction bag was initially divided into two subchambers, with O_3 being injected into one subchamber and the organic into the other. The reactions were initiated by removing the bag divider and rapidly mixing the contents of the bag by pushing down on alternate sides of the entire bag for ~1 minute. Initial O_3 concentrations after mixing were typically ~1 ppm (1 ppm = 2.41×10^{13} molecule cm^{-3} at 295 K and 735 torr total pressure) and, after mixing of the reactants, the O_3 concentrations were monitored by a Monitor Labs Model 8410 chemiluminescence ozone analyzer as a function of time. Background ozone decay rates in the absence of a reactant were determined periodically during these rate constant determinations, and were in the range $(0.1-3.5) \times 10^{-5}$ sec^{-1}.

The concentrations of <u>cis</u>- and <u>trans</u>-1,3-dichloropropene were calculated from the known amounts of these reactants introduced into the reaction bag and the volume of the reaction bag.

For the measurement of the rate constants for reaction with OH radicals, a relative rate technique was used, which has also been described in detail previously (Atkinson et al. 1981b, 1982b,c, 1983b). Hydroxyl radicals were generated by the photolysis, at wavelengths $\gtrsim$290 nm, of methyl nitrite in air at ppm concentrations:

$$CH_3ONO + h\nu \rightarrow CH_3O + NO$$

$$CH_3O + O_2 \rightarrow HCHO + HO_2$$

$$HO_2 + NO \rightarrow OH + NO_2$$

In order to minimize the formation of O_3 during these irradiations, NO was included in the reaction mixtures. In the presence of reactant and reference organics, the OH radicals can, besides reacting with CH_3ONO, NO, NO_2, and the organic reaction products, react with these organics:

$$\mathrm{OH + reactant \rightarrow products} \tag{3}$$

$$\mathrm{OH + reference\ organic \rightarrow products} \tag{4}$$

Providing the organics are consumed only by reaction with OH radicals (see later), and since dilution due to sampling is avoided by use of a collapsible Teflon reaction bag, then

$$\frac{-d\ln[\mathrm{reactant}]}{dt} = k_3[\mathrm{OH}] \tag{III}$$

and

$$\frac{-d\ln[\mathrm{reference\ organic}]}{dt} = k_4[\mathrm{OH}] \tag{IV}$$

where k_3 and k_4 are the rate constants for reactions (3) and (4), respectively. Hence

$$\ln\left(\frac{[\mathrm{reactant}]_{t_o}}{[\mathrm{reactant}]_t}\right) = \frac{k_3}{k_4}\ln\left(\frac{[\mathrm{reference\ organic}]_{t_o}}{[\mathrm{reference\ organic}]_t}\right) \tag{V}$$

where $[\mathrm{reactant}]_{t_o}$ and $[\mathrm{reference\ organic}]_{t_o}$ are the concentrations of the reactant and reference organic, respectively, at time t_o, and $[\mathrm{reactant}]_t$ and $[\mathrm{reference\ organic}]_t$ are the corresponding concentrations at time t. Thus plots of $\ln([\mathrm{reactant}]_{t_o}/[\mathrm{reactant}]_t)$ against $\ln([\mathrm{reference\ organic}]_{t_o}/[\mathrm{reference\ organic}]_t)$ should yield straight lines of slope k_3/k_4 and zero intercept.

For these relative rate measurements irradiations were carried out in an ~60-ℓ FEP Teflon cylindrical reaction bag surrounded by 24 GE F15T8-BL 15-W blacklights. In this work, 8 or 16 of these blacklights were used, corresponding to a photolytic half-life of CH_3ONO of ~30 or ~20 min, respectively. Prior to irradiation, the reaction bag/lamp assembly was covered to avoid any photolysis of the reactants.

The reference organic chosen was n-octane. These organics were quantitatively monitored prior to, and during, the irradiations by gas chromatography with flame ionization detection (GC-FID), using a 20-ft x 0.125-in. stainless steel column packed with 5% DC703/C20M on 110/120 mesh AW, DMCS Chromosorb G, operated at 60°C. NO, NO_x, and O_3 were monitored by chemiluminescence instruments. Initial reactant concentrations employed in these irradiations were: CH_3ONO, ~5 ppm; NO, ~5 ppm; and ~1 ppm each of the reference and reactant organics. Ultra-zero air (Liquid Carbonic, <0.1 ppm hydrocarbons) was used as the diluent gas. All rate constant determinations were carried out at 295 ± 2 K and atmospheric pressure (~735 torr).

2. Environmental Chamber Experiments

In order to identify the major products and obtain estimates of their yields from the reactions of cis- and trans-1,3-dichloropropene with O_3 and OH radicals, experiments were conducted in air at ppm concentrations of the reactants in an environmental chamber with analysis of gas phase species by in situ long-path FT-IR spectroscopy.

The reaction chamber was an evacuable, thermostatted 5800-ℓ aluminum cylinder with Teflon-coated inner walls, both ends of which were fitted with a grid of quartz panes to permit full illumination by a solar simulator which derived radiation from a 25 KW high-pressure Xe lamp (Winer et al. 1980). The chamber was equipped along its longitudinal axis with a set of gold-coated, multiple-reflection optics with a base path of 1.3 m. The long-path optics were interfaced to an Eocom infrared interferometer which was equipped with a liquid-N_2 cooled HgCdTe detector and controlled by a Nicolet 1180 data system.

A total pathlength of 62.9 m and spectral resolution of 1 cm^{-1} were employed throughout the experiments. Data collection consisted of co-adding 64 interferograms (64 scans) per calculated spectrum, which allowed spectra to be recorded conveniently every three minutes when desired. At the end of an experiment, each spectrum was ratioed against a background spectrum and converted to the absorbance form. Derivation of quantitative information from the spectra was facilitated by spectral desynthesis (i.e., successive subtraction of absorptions by known compounds using calibrated reference spectra).

For the O_3 reaction experiments, the initial concentrations were ~10 ppm of the trans- or cis-1,3-dichloropropene and ~5 ppm O_3, with air as the diluent gas. For the OH radical reactions, irradiations were carried out using a mixture of ~10 ppm each of the dichloropropene, CH_3ONO, and NO, with air as the diluent gas. Partial pressures of CH_3ONO, NO, and the 1,3-dichloropropene vapors were measured into calibrated glass bulbs (0.05-5 ℓ) with an MKS Baratron capacitance manometer and brought to atmospheric pressure with ultra-high purity N_2. These pre-determined amounts of reactants were flushed with high-purity N_2 into the reaction chamber with rapid mixing by fans.

3. Materials

Samples of trans- and cis-$CH_2ClCH{=}CHCl$ were procured from Pfaltz and Bauer. A combination of GC and FT-IR analyses revealed that vapors of the trans sample, from the liquid thermostatted at 296 K, consisted of 85.0% of the trans-isomer and 15.0% of the cis-isomer; those of the cis sample were found to contain 64.5% of the cis form, 15.1% of the trans form, and 20.4% of 1,2-dichloropropane. Attempts at purification indicated that an extremely efficient distillation column would be required to attain a complete separation of the isomers. Thus, the commercial samples were used without further purification since both GC and FT-IR analyses could distinguish the changes in the concentrations of the components and since 1,2-dichloropropane was essentially unreactive in the particular chemical systems employed.

CH_3ONO was prepared by dropwise addition of 50% H_2SO_4 to a saturated solution of $NaNO_2$ in CH_3OH and purified according to published procedures (Taylor et al. 1980). Nitric oxide (99.0%) was supplied by the Matheson Gas Company. Ozone was produced in a Welsbach T-408 generator at a pre-calibrated voltage and input flow of high-purity O_2 (Liquid Carbonic, 99.995%) and collected in calibrated flasks. The concentrations of O_3 samples were verified by infrared spectroscopic analysis of samples simultaneously collected in a 10-cm cell.

C. Results

1. Rate Constants for Reaction with Ozone

In all cases, the O_3 decays monitored in the presence of varying concentrations of cis- and trans-1,3-dichloropropene were exponential within the experimental errors, as shown by the linearity of plots of $\ln([O_3]_{t_o}/[O_3]_t)$ against time $(t-t_o)$, where $[O_3]_{t_o}$ and $[O_3]_t$ are the O_3 concentrations at times t_o and t, and t_o is the time after mixing of the reactants is complete. The O_3 decay rates, obtained by least squares analyses of the slopes of such plots, increased linearly with the gas phase concentration of the reactants, as shown in Figure II-1.

For the pure cis- and trans-isomers of 1,3-dichloropropene, the slopes of these plots would yield the rate constants k_2 directly. However, as noted in the Experimental section, for cis- and trans-1,3-dichloropropene these samples were not those of the pure isomers. When the slopes of the plots in Figure II-1 were corrected according to the isomer ratios as determined by GC and FT-IR analyses (see Experimental section), values of

$$k_2 \text{ (cis-dichloropropene)} = (1.5 \pm 0.5) \times 10^{-19} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$$

and

$$k_2 \text{ (trans-dichloropropene)} = (6.7 \pm 0.8) \times 10^{-19} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$$

were derived at 295 ± 2 K, where the indicated errors are two least squares standard deviations combined with an estimated overall uncertainty of 10% in the 1,3-dichloropropene concentrations in the reaction bag. The presence of significant amounts of 1,2-dichloropropane in the cis sample did not affect the above results, since this impurity was shown to be unreactive towards O_3 (cf. below).

2. Rate Constants for Reaction with Hydroxyl Radicals

Irradiations of CH_3ONO/NO/n-octane/cis- and trans-1,3-dichloropropene/air mixtures were carried out, with the irradiation times ranging from 15-45 min. n-Octane was used as the reference organic (Atkinson et al. 1982d). Plots of equation (V) are shown in Figure II-2, and least squares analyses of these data yield the rate constant ratios given in Table II-1. With this technique, since the disappearance of the cis- and trans-1,3-dichloropropene isomers were monitored directly by GC, the rate constant ratios given in Table II-1 correspond directly to those for these isomers, in contrast to the situation for the O_3 reactions discussed above.

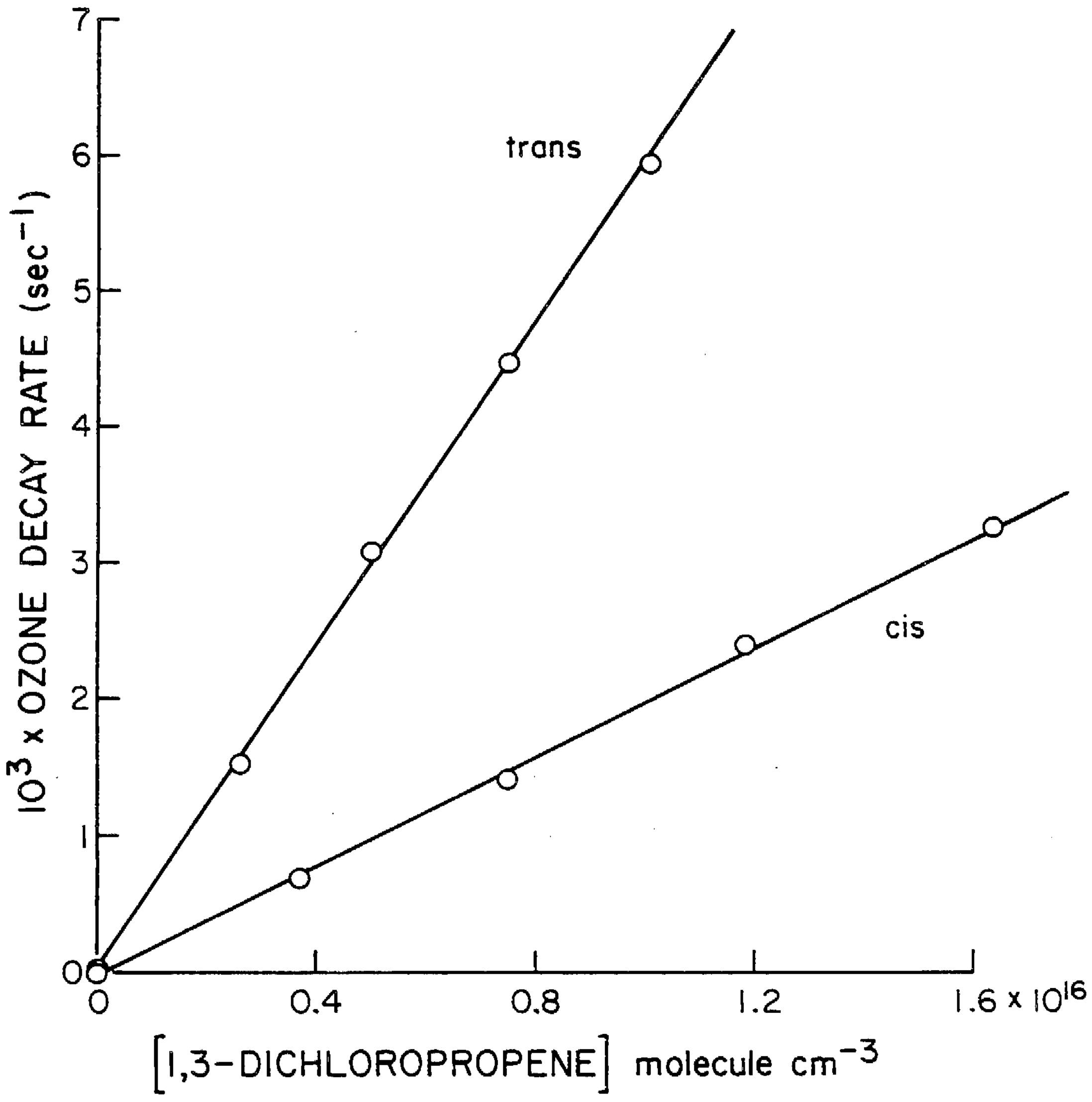


Figure II-1. Plot of equation (II) for the reactions of the trans- and cis-$ClCH_2CH=CHCl$ samples with O_3.

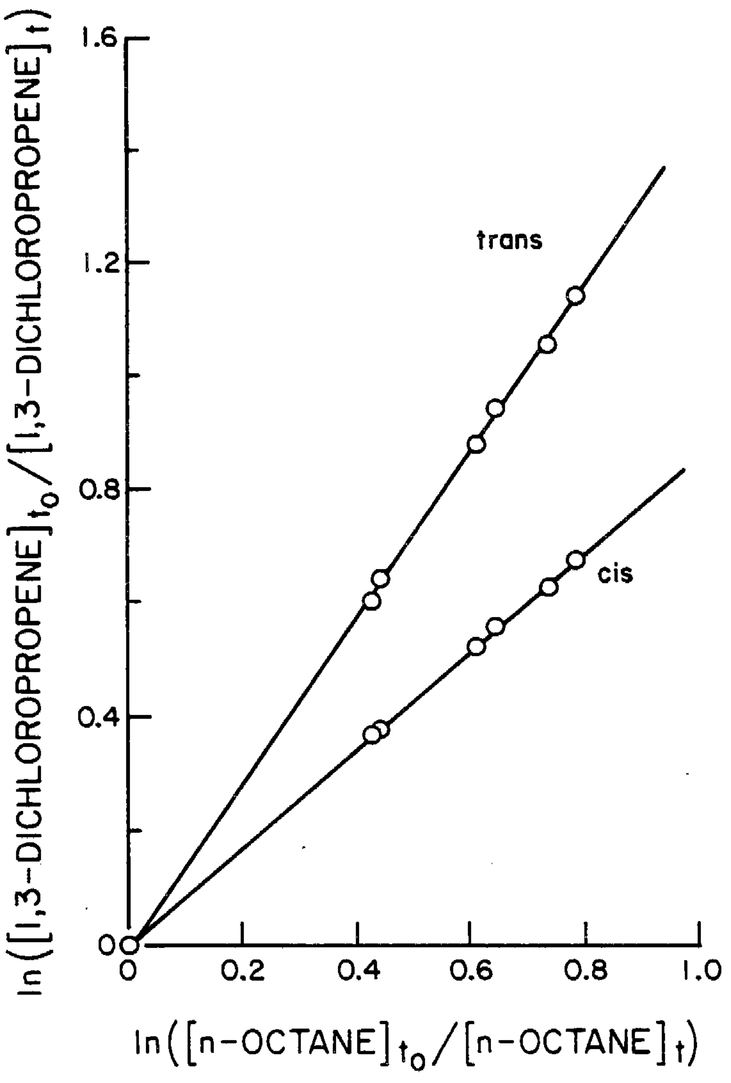


Figure II-2. Plot of equation (V) for the reactions of OH radicals with _cis_- and _trans_-$ClCH_2CH=CHCl$ and n-octane.

Table II-1. Rate Constant Ratios k_3/k_4 and Rate Constants k_3 for the Reaction of OH Radicals with *cis*- and *trans*-1,3-Dichloropropene at 295 ± 2 K

Reactant	k_3/k_4[a]	$10^{11} \times k_3$ (cm^3 $molecule^{-1}$ sec^{-1})[b]
cis-1,3-Dichloropropene	0.859 ± 0.013	0.774 ± 0.020
trans-1,3-Dichloropropane	1.45 ± 0.04	1.31 ± 0.05

[a] Error limits are two least squares standard deviations of the slopes of the plots shown in Figure II-2.

[b] Relative to k(OH + *n*-octane). Placed on an absolute basis using a rate constant for this reaction of (9.01 ± 0.19) x 10^{-12} cm^3 $molecule^{-1}$ sec^{-1} (Atkinson et al. 1982d). The error limits are two least squares standard deviations.

These rate constant ratios can be placed on an absolute basis using the literature rate constants for the reaction of OH radicals with *n*-octane (Atkinson et al. 1982d). The rate constants k_3 so derived are also given in Table II-1.

3. FT-IR Spectroscopic Studies

In situ, long-path FT-IR spectroscopy was employed to characterize the major products formed in the reactions of *cis*- and *trans*-1,3-dichloropropene with O_3 and OH radicals. As discussed above, the experiments were conducted in the 5800-ℓ environmental chamber at ppm concentrations of the reactants in air at room temperature (~296 K) and pressure (~730 torr).

The major products which were positively identified in the reaction of O_3 with 1,3-dichloropropene were formyl chloride ($H\overset{\overset{O}{\|}}{C}Cl$) and chloroacetaldehyde ($ClCH_2CHO$). Figure II-3A shows the infrared spectrum of the reaction mixture with initial concentrations of 8.99 ppm *trans*-/1.79 ppm *cis*-$CH_2ClCH{=}CHCl$ (from the commercial *trans* sample) and 5.3 ppm O_3 in air after 38 min of reaction. Subtraction of the absorptions of unreacted *trans*- and *cis*-$CH_2ClCH{=}CHCl$ and O_3 in Figure II-3B shows that the dominant feature of the product spectrum is the formyl chloride absorption at 1784 cm^{-1}. [Formyl chloride was generated from the reaction of 10 ppm *trans*-1,2-dichloroethene with 5 ppm O_3 in air (Hisatsune and Heicklen 1973).

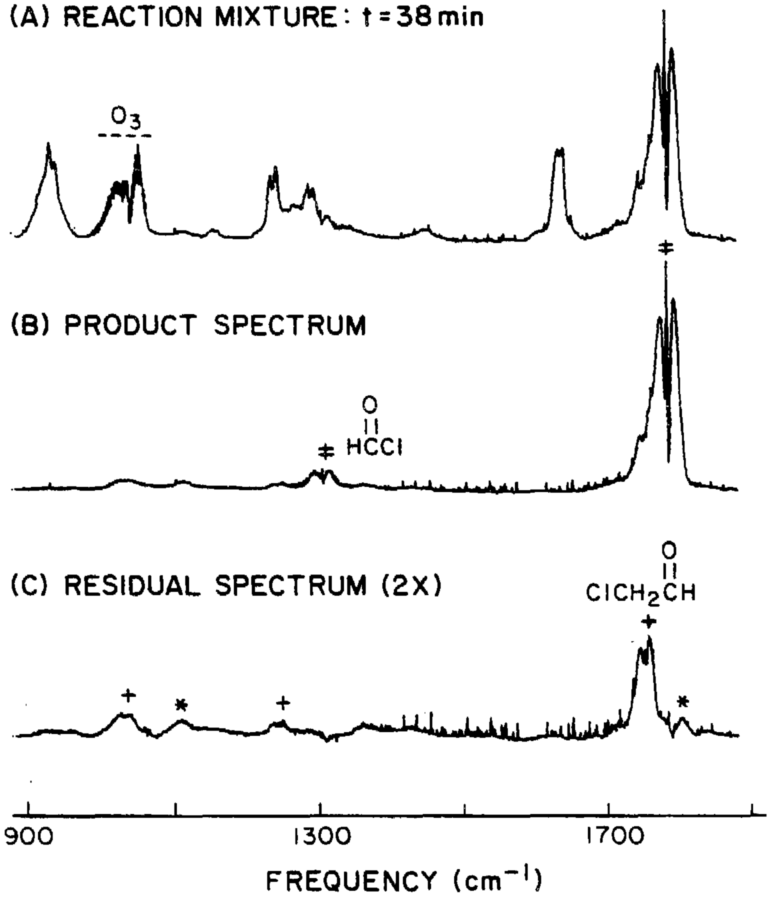


Figure II-3. (A) Infrared spectrum of the reaction mixture initially containing 8.99 trans-/1.79 ppm cis-$ClCH_2CH=CHCl$ and 5.3 ppm O_3.

(B) Product spectrum minus the absorptions of reactants.

(C) Expanded (2X) residual spectrum after subtraction of HC(O)Cl bands; * - probable absorption bands of $ClCH_2COOH$.

Reference spectra were derived from the first 20 min of this reaction which showed a linear plot of the formyl chloride absorbance versus the amount of trans-1,2-dichloroethene consumed. Calibration was based on an assumed 1:1 stoichiometric yield (Herron et al. 1982, Niki et al. 1982).] After subtraction of the formyl chloride absorptions, the identifying bands of chloroacetaldehyde, particularly its strongest absorption at 1751 cm^{-1}, can be seen in the expanded (2X) scale of Figure II-3C.

Although less definitive, chloroacetic acid ($ClCH_2COOH$) appears to be a significant product of the dichloropropene-O_3 reaction. The vapor-phase spectrum recorded from an authentic sample had identifying features comprised of two weak, broad absorptions at ~1115 cm^{-1} and ~1795 cm^{-1}. Evidence that this species was formed is provided by bands marked with "*" in the residual spectrum of Figure II-3C. Upper limit estimates from the spectra indicated ~0.2 $ClCH_2COOH$ formed per 1,3-dichloropropene consumed throughout the reaction; ~0.53 ppm of $ClCH_2COOH$ was calculated to be present at t = 38 min [spectrum (C) of Figure II-3].

Figure II-4 shows the concentration-time plots of the reactants and the products formyl chloride and chloroacetaldehyde for the reaction of dichloropropene with O_3. In agreement with the results of kinetic experiments, Figure II-4 shows that the trans-isomer reacted much faster than the cis-isomer. The O_3 decay rate was much faster during the initial stage of the reaction (i.e., $\leq$3 min) with ~1.5 O_3 consumed per dichloropropene (total of both isomers) consumed; thereafter, this ratio decreased to ~0.6 for the major portion of the reaction, suggesting that there were loss processes for dichloropropene other than reaction with O_3. The chloroacetaldehyde yield per dichloropropene consumed was ~0.4 throughout the reaction; the yield of formyl chloride per dichloropropene showed a decrease from a value of ~0.7 at t = 8 min to ~0.55 at t = 63 min. The latter may be due to the instability of formyl chloride since it is known to decompose and react with H_2O to form HCl, CO, and HCOOH (Hisatsune and Heicklen 1973). In addition to the observed formation of HCl, CO, CO_2, and HCOOH, other weak and broad absorption features were evident in the product spectra due to as yet unidentified species.

An experiment was also carried out for the commercial cis sample, with the initial reaction mixture consisting of 6.67 ppm cis-$ClCH_2CH=CHCl$, 1.67 ppm trans-$ClCH_2CH=CHCl$, 1.93 ppm $CH_3CHClCH_2Cl$, and 5.47 ppm O_3.

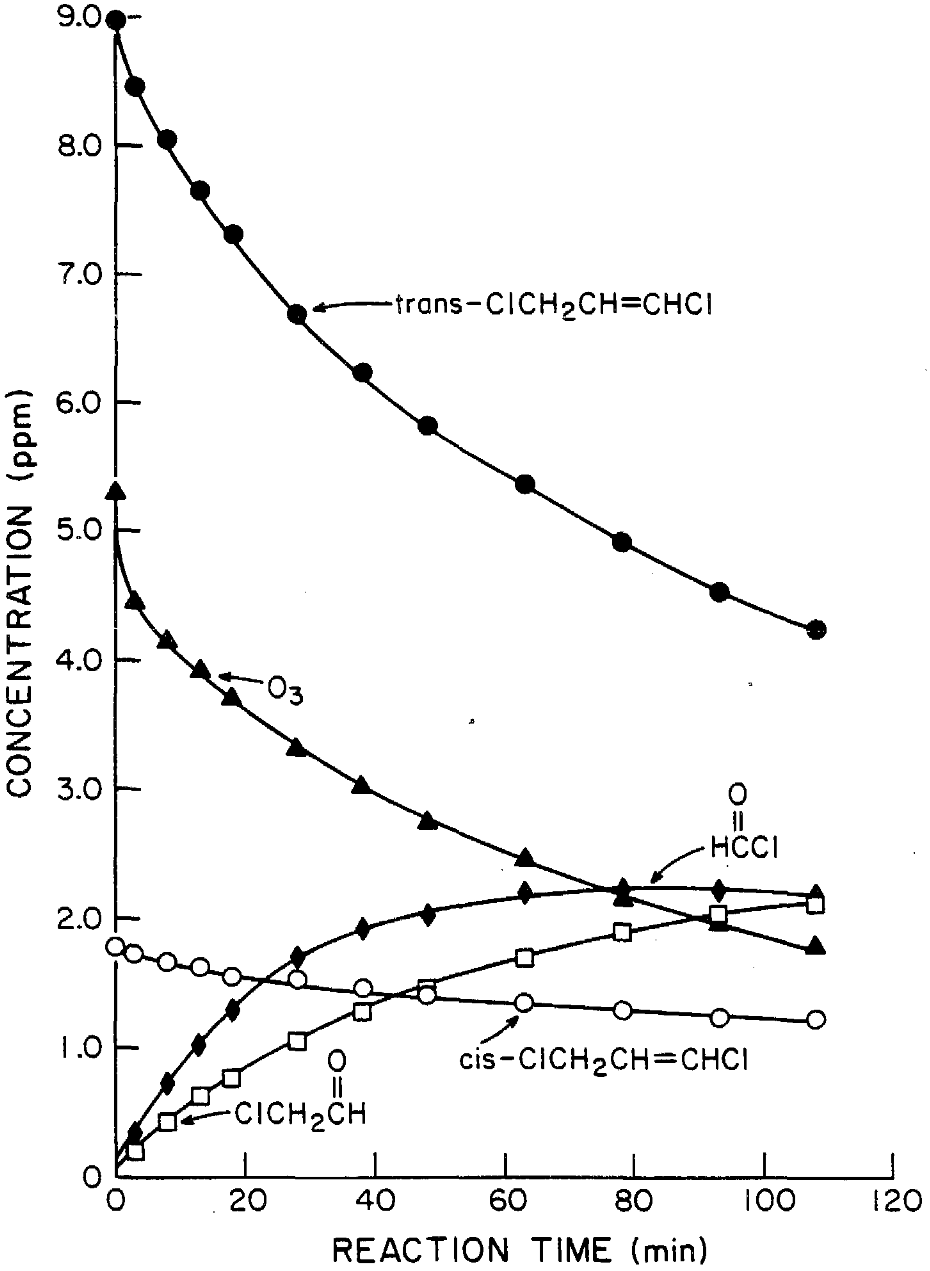


Figure II-4. Time-concentration profiles of reactants and products from an air mixture of the trans-$ClCH_2CH=CHCl$ sample and O_3.

Although, as expected, this reaction proceeded at a much slower rate than that for the *trans* sample, identical products were formed with generally similar stoichiometries. The 1,2-dichloropropane was totally unreactive in this system, undergoing no detectable change during the 145-minute reaction time.

In the study of the reaction of OH radicals with *cis*- and *trans*-dichloropropene, photolyses of CH_3ONO/NO mixtures in air were employed to generate OH radicals. This method has been shown to be a convenient and efficient source of OH radicals for kinetic studies (Atkinson et al. 1981b, 1982b,c, 1983b). In the present system, however, additional spectral subtraction involving the known CH_3ONO/NO photolysis products (CH_3ONO_2, HCHO, HNO_3, and NO_2) had to be carried out to identify the products arising from the reaction of OH radicals with 1,2-dichloropropane. In order to minimize the effects of secondary reactions, quantitative information was derived from data obtained at short irradiation times.

The experiment for the commercial *trans* sample had initial concentrations of 8.55 ppm *trans*- and 1.48 ppm *cis*-$CH_2ClCH{=}CHCl$ and 10 ppm each of CH_3ONO and NO. The infrared spectrum recorded after 5 min of irradiation revealed the loss of 2.37 ppm of dichloropropene (2.34 ppm of the *trans*-isomer + 0.03 ppm of the *cis*-isomer) and formation of 2.15 ppm of $H\overset{O}{\overset{\|}{C}}Cl$ and 2.22 ppm of $ClCH_2CHO$. At 15 min into the irradiation, the corresponding yields were 3.22 ppm of $H\overset{O}{\overset{\|}{C}}Cl$ and 3.45 ppm of $ClCH_2CHO$ for 3.84 ppm of dichloropropene consumed.

An irradiation of the commercial *cis* sample was also carried out, with initial concentrations of 6.60 ppm *cis*- and 1.52 ppm *trans*-$CH_2ClCH{=}CHCl$, 10 ppm CH_3ONO, and 10 ppm NO. The results were identical to those for the *trans* sample, the stoichiometry being one molecule each of formyl chloride and chloroacetaldehyde formed per molecule of reacted dichloropropene.

During the irradiation of the *cis* sample, the concentration of the 1,2-dichloropropane impurity showed very little change. The rate of the reaction of OH radicals with 1,2-dichloropropane was investigated further by carrying out a separate irradiation of a mixture of 10 ppm each of $CH_3CHClCH_2Cl$, CH_3OCH_3, CH_3ONO, and NO in one atmosphere of air. The added CH_3OCH_3 served as the reference compound with a well established OH radical rate constant (Perry et al. 1977a). Although no products arising from 1,2-dichloropropane could be identified, a maximum loss of ~5% was estimated for this compound during the 60-min irradiation in which a 29.1% loss of CH_3OCH_3 was observed. From the literature value for the OH radical rate constant of CH_3OCH_3 of $(3.5 \pm 0.35) \times 10^{-12}$ cm^3 $molecule^{-1}$ sec^{-1} (Perry et al. 1977a), the above results yield an upper limit OH radical reaction rate constant of $\lesssim 6 \times 10^{-13}$ cm^3 $molecule^{-1}$ sec^{-1} for 1,2-dichloropropane at room temperature.

D. Discussion

1. Reactions with OH Radicals

The observed formation of one molecule each of formyl chloride and chloroacetaldehyde, per molecule of 1,3-dichloropropene reacting with OH radicals, indicates that the initial reaction proceeds almost exclusively via OH addition to either carbon of the double bond. This is consistent with the well-studied case of the OH radical reaction with propene (Atkinson et al. 1979, Biermann et al. 1982, Atkinson and Lloyd 1984) where $\gtrsim 95\%$ of the total reaction was shown to proceed via OH radical addition to the olefinic double bond.

Figure II-5 illustrates the reaction scheme proposed for the reaction of OH radicals with 1,3-dichloropropene. In this reaction sequence, the initially-formed adduct radicals react rapidly with O_2 to form the corresponding chlorine substituted alkylperoxy radicals. In the presence of NO, the peroxy radicals yield the respective alkoxy intermediates plus NO_2. Scission of the alkoxy radical leads to the formation of the hydroxychloroalkyl radical together with the corresponding aldehyde, and further reaction of the hydroxychloroalkyl radical with O_2 completes the reaction, forming one molecule each of $H\overset{\overset{O}{\|}}{C}Cl$ and $ClCH_2CHO$ from either mode of OH radical addition.

2. Reactions with Ozone

The product distribution observed in the reaction of O_3 with dichloropropene suggests a more complicated mechanism than that for the OH radical reaction. Results of previous studies on the gas-phase ozonolysis of alkenes (Martinez et al. 1981, Atkinson and Lloyd 1984) and chloroethylenes (Niki et al. 1982) have demonstrated that complex product

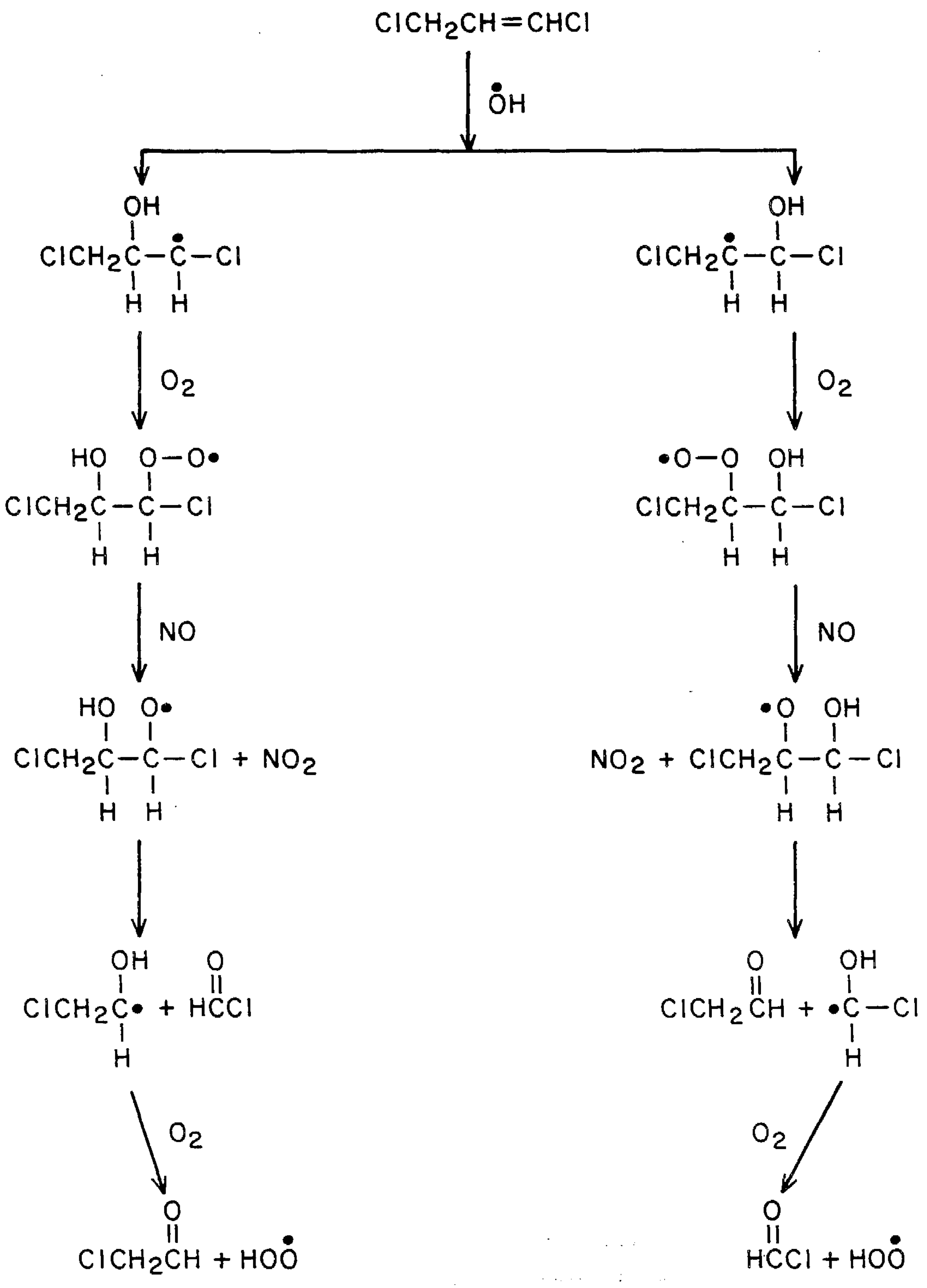


Figure II-5. Mechanism for the reaction of $ClCH_2CH{=}CHCl$ with the OH radical.

stoichiometries and mechanisms are involved in these reactions, and a general scheme is presented for the reaction of O_3 with 1,3-dichloropropene in Figure II-6.

It is generally accepted that a trioxolane or primary ozonide (**A** in Figure II-6) is initially formed during the ozonolysis of alkenes, which then rapidly decomposes (Harding and Goddard 1978, Herron et al. 1982, Atkinson and Lloyd 1984). The two decomposition pathways result in the production of formyl chloride and chloroacetaldehyde, along with the "Criegee intermediates" **B** and **C** (Criegee 1975) which initially contain excess energy resulting from the reaction exothermicities.

The ensuing fate of the Criegee intermediates is the most uncertain aspect of these mechanisms. The initially energy-rich biradicals **B** and **C** may undergo immediate decomposition, rearrangement, or thermalization followed by further reaction with other species (Herron et al. 1982, Atkinson and Lloyd 1984). Chloroacetic acid is most likely produced by a rearrangement of **B**, but it is believed to be initially in an energy-rich state and can further decompose as well as be collisionally deactivated (Herron et al. 1982, Atkinson and Lloyd 1984). Apart from CO and CO_2, no other likely decomposition products arising from **B** have been identified in the present study.

By analogy with the formation of $ClCH_2COOH$ from **B**, ClCOOH could also have been formed from **C**. Its nondetection is attributed to its known rapid decomposition to CO_2 and HCl at room temperature (Jensen and Pimentel 1967). Evidence from the study of the reactions of O_3 with the chloroethylenes (Niki et al. 1982) also suggests that the thermally active intermediate **C** undergoes unimolecular dissociation to produce CO, CO_2, H, Cl, and OH fragments. The secondary reactions involving these radicals almost certainly contribute to kinetic and mechanistic complications (Niki et al. 1982). Indeed, the values of k_2 must be rigorously considered to be upper limits to the actual rate constants, although at the high [reactant]/[O_3] ratios used ($\geq$100 for <u>cis</u>- and <u>trans</u>-dichloropropene) any Cl atoms produced would react essentially totally with the reactant organic, thus minimizing secondary reactions with O_3. Additional detailed experiments which are required to define the effects of these secondary reactions in the 1,3-dichloropropene-O_3 system were beyond the scope of the present investigation. Nevertheless, the major products which have

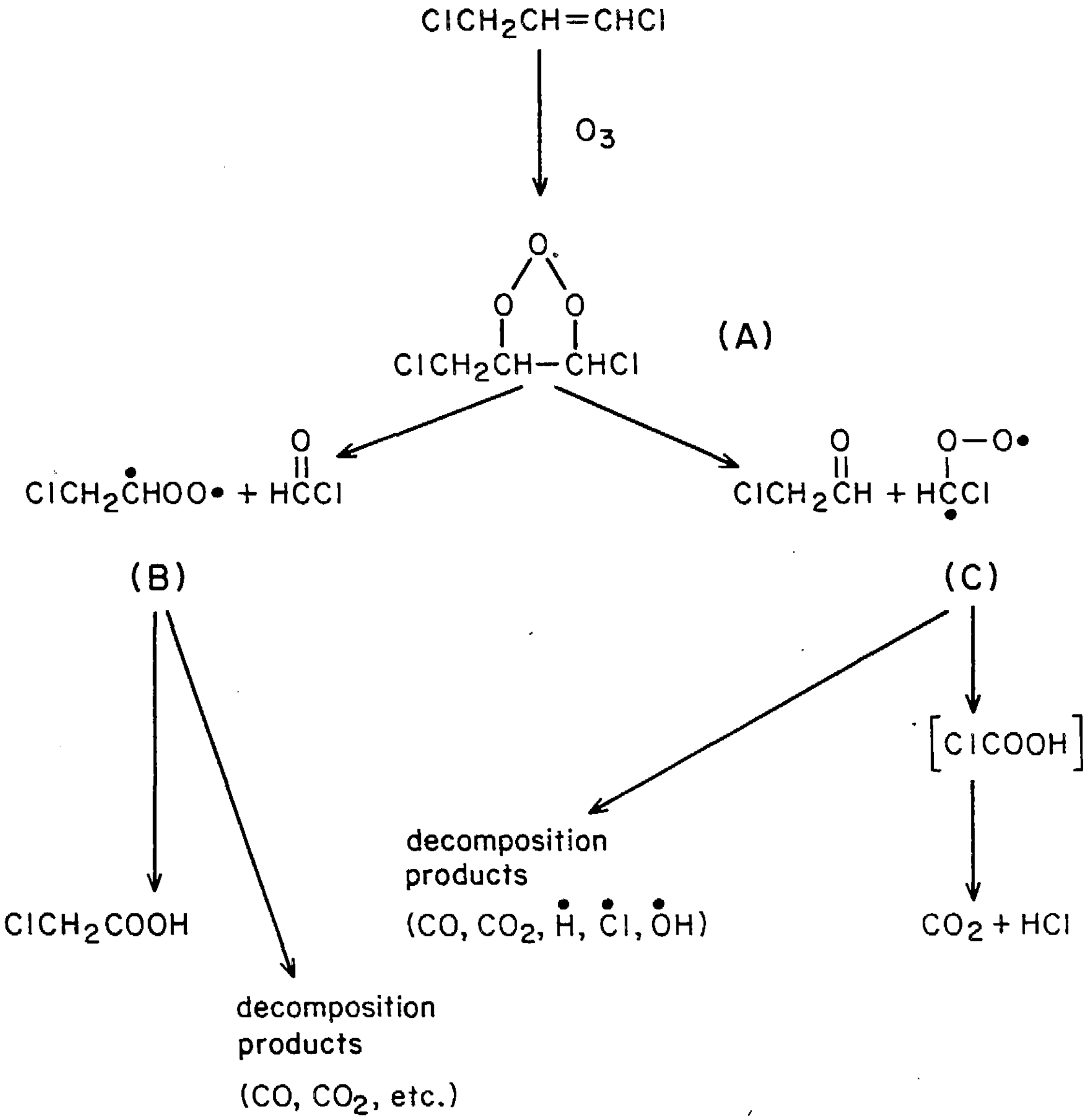


Figure II-6. General mechanism for the reaction of $ClCH_2CH=CHCl$ with O_3 reaction.

been identified here from the reaction of O_3 with 1,3-dichloropropene are consistent with the general features of the currently accepted alkene-O_3 reaction mechanism.

The kinetic data obtained in this work, together with the available literature data, allow the effects of chlorine atom substitution on olefinic double bonds to be assessed for both O_3 and OH radical reactions. As shown in Table II-2, Cl atom substitution, even when the position of substitution is not on the double bond, markedly decreases the reactivity towards O_3, with a smaller effect on the reactivity towards the OH radical.

The measured rate constants for the reactions with O_3 and the OH radical allow estimates to be made of the lifetimes of 1,3-dichloropropene

Table II-2. Kinetic Data at Room Temperature for the Reactions of O_3 and OH Radicals with Chlorine-Containing Alkenes

Alkene	Rate constant (in cm^3 $molecule^{-1}$ sec^{-1} units)	
	O_3[a]	OH[b]
$CH_2=CH_2$	1.8×10^{-18}	8.5×10^{-12}
$CH_2=CHCl$	2.5×10^{-19}	6.6×10^{-12}
$CH_2=CCl_2$	3.7×10^{-21}	-
<u>cis</u>-CHCl=CHCl	$<5 \times 10^{-21}$	-
<u>trans</u>-CHCl=CHCl	1.8×10^{-19}	-
$CHCl=CCl_2$	$<3 \times 10^{-20}$	2.4×10^{-12}
$CCl_2=CCl_2$	$<2 \times 10^{-23}$	1.7×10^{-13}
$CH_3CH=CH_2$	1.1×10^{-17}	2.5×10^{-11}
<u>cis</u>-$CH_2ClCH=CHCl$	1.5×10^{-19}[c]	7.7×10^{-12}[c]
<u>trans</u>-$CH_2ClCH=CHCl$	6.7×10^{-19}[c]	1.3×10^{-11}[c]
$CH_2=C(CH_3)_2$	1.2×10^{-17}	5.1×10^{-11}
$CH_2=C(CH_2Cl)_2$	3.9×10^{-19}	3.8×10^{-11}

[a] From Atkinson and Carter (1984) except as noted.
[b] From Atkinson et al. (1979, 1982b), except as noted.
[c] This work.

with respect to these atmospheric removal processes. Based on a background tropospheric O_3 concentration of ~1 x 10^{12} cm^{-3} (~0.04 ppm) (Singh et al. 1978), the half-lives with respect to reaction with O_3 are calculated to be 12 days and 52 days, respectively, for the *trans*- and *cis*-isomers. Likewise, based on an estimated daytime OH radical concentration of ~2 x 10^6 cm^{-3} (~8 x 10^{-8} ppm) (Crutzen 1982), the half-lives with respect to reaction with the OH radical are respectively 7 hr and 12 hr for the *trans* and *cis* forms. The experiments also indicated that the only significant loss process for 1,2-dichloropropane in the atmosphere would be reaction with OH radicals, for which a half-life of ≥13 days is estimated for a 24-hr average OH radical concentration of 1 x 10^6 cm^{-3}. This result is of interest since 1,2-dichloropropane, along with the *cis*- and *trans*-1,3-dichloropropenes, is an important component of the fumigant formulations D-D and Telone.

It is obvious that the above estimates of lifetimes for reactions with O_3 and OH radicals are necessary inputs in assessing the impact of 1,3-dichloropropene released into the atmosphere as a result of its wide use as an agricultural chemical. Additional important data should, however, be considered concerning the photodegradation of this compound. Thus, although the rate of photolysis of 1,3-dichloropropene in air appears insignificant relative to the above reactions, experimental evidence exists (Moilanen et al. 1975) that photodecomposition could be highly enhanced in the presence of atmospheric particulates.

Lastly, in evaluating the possible harmful effects of 1,3-dichloropropene, it would be prudent as well to consider the potential health risks associated with the products $H\overset{\overset{O}{\|}}{C}Cl$, $ClCH_2CHO$, and $ClCH_2COOH$. Whereas formyl chloride is known to eventually decompose and hydrolyze to CO, HCl, and HCOOH, the other toxic products chloroacetyladehyde and chloroacetic acid may actually persist appreciably longer in the environment. Whether the ambient levels of these products could ever be sufficiently high, under normal use of the parent compounds, to be of concern remains to be determined.

III. ATMOSPHERIC CHEMISTRY OF THE TOXIC CHLOROETHYLENES VINYL CHLORIDE, TRICHLOROETHYLENE AND TETRACHLOROETHYLENE

The chloroethylenes vinyl chloride (CH_2=CHCl), trichloroethylene (CHCl=CCl_2) and tetrachloroethylene (CCl_2=CCl_2) are widely used as industrial chemicals (vinyl chloride) or as solvents (tri- and tetrachloroethylene), and have been monitored at ppb levels in urban areas (Singh et al. 1981). Furthermore, these three chloroethylenes are either carcinogenic or suspected carcinogens. A previous study of the photooxidations of these and other chloroethylenes by Gay et al. (1976) has identified some of the products. However, a more detailed experimental study concerning the mechanisms and products of the atmospherically important reactions of these compounds was needed.

The available kinetic data concerning the reactions of these three chloroethylenes with O_3 (Atkinson and Carter 1984) and OH radicals (Atkinson et al. 1979) show that, under atmospheric conditions, they will react essentially solely with the OH radical. Hence in this study we have investigated, using in situ long pathlength Fourier transform infrared (FT-IR) absorption spectroscopy, the products and mechanisms of the OH radical reactions with vinyl chloride, trichloroethylene and tetrachloroethylene (referred to henceforth as trichloroethene and tetrachloroethene, respectively).

A. Experimental

NO_x-air photooxidations of the three chloroethylenes (referred to henceforth as chloroethenes) were carried out in two environmental chambers. One was a 3700-ℓ all-Teflon chamber equipped with blacklight irradiation, and the other was the SAPRC 5800-ℓ evacuable, Teflon-coated environmental chamber, with irradiation being provided by a 25 KW Xenon arc (Winer et al. 1980). Both chambers were equipped with a set of multiple-reflection White-type optical systems, with base paths of 1.99 m for the all-Teflon chamber and 1.33 m for the evacuable chamber. These sets of multiple-reflection optics were interfaced to an FT-IR spectrometer. The reactants and products were monitored by FT-IR absorption spectroscopy, using ~60-meter pathlengths and a spectral resolution (unapodized) of 1 cm^{-1}.

Hydroxyl radicals were generated by the photolysis of methyl nitrite in air at wavelengths $\gtrsim$290 nm

$$CH_3ONO + h\nu \rightarrow CH_3O + NO$$

$$CH_3O + O_2 \rightarrow HCHO + HO_2$$

$$HO_2 + NO \rightarrow OH + NO_2$$

NO was included in the reaction mixtures in order to minimize the formation of O_3 and of NO_3 radicals. The initial concentrations of the CH_3ONO-NO-chloroethene-air mixtures were: CH_3ONO ~10 ppm, NO ~5-10 ppm, chloroethene ~6-13 ppm, with one atmosphere of dry pure matrix air for the experiments in the 3700-ℓ all-Teflon chamber or of synthetic air (80% N_2 + 20% O_2) for the 5800-ℓ evacuable chamber experiments.

The absorption frequencies (cm^{-1}) used for monitoring the reactants and products were as follows: vinyl chloride, 942.1 and 1610.8; trichloroethene, 849.5 and 945.1; tetrachloroethene, 916.0; formyl chloride, 738.7 and 1783.4; phosgene, 849.6. Reference spectra of these compounds are presented in Figures III-1 and III-2.

All experiments were carried out at atmospheric pressure (~740 torr) and 298 ± 2 K.

B. Results

A series of irradiations of CH_3ONO-NO-chloroethene-air mixtures were carried out in both the 3700-ℓ all-Teflon chamber and in the SAPRC 5800-ℓ evacuable chamber. The concentrations of the chloroethenes and of the products are given in Tables III-1 to III-3.

Irradiation times ranged from ~15 min for vinyl chloride to 25-28 min for trichloroethene and 40-60 min for tetrachloroethene; these were inversely correlated with the OH radical rate constants (Atkinson et al. 1979). Due to the use of methyl nitrite as a precursor to OH radicals, formaldehyde could not be quantified as a product from the CH_3ONO-NO-air photooxidation of vinyl chloride by FT-IR spectroscopy. The data in Tables III-1 to III-3 show that the products observed and quantified were

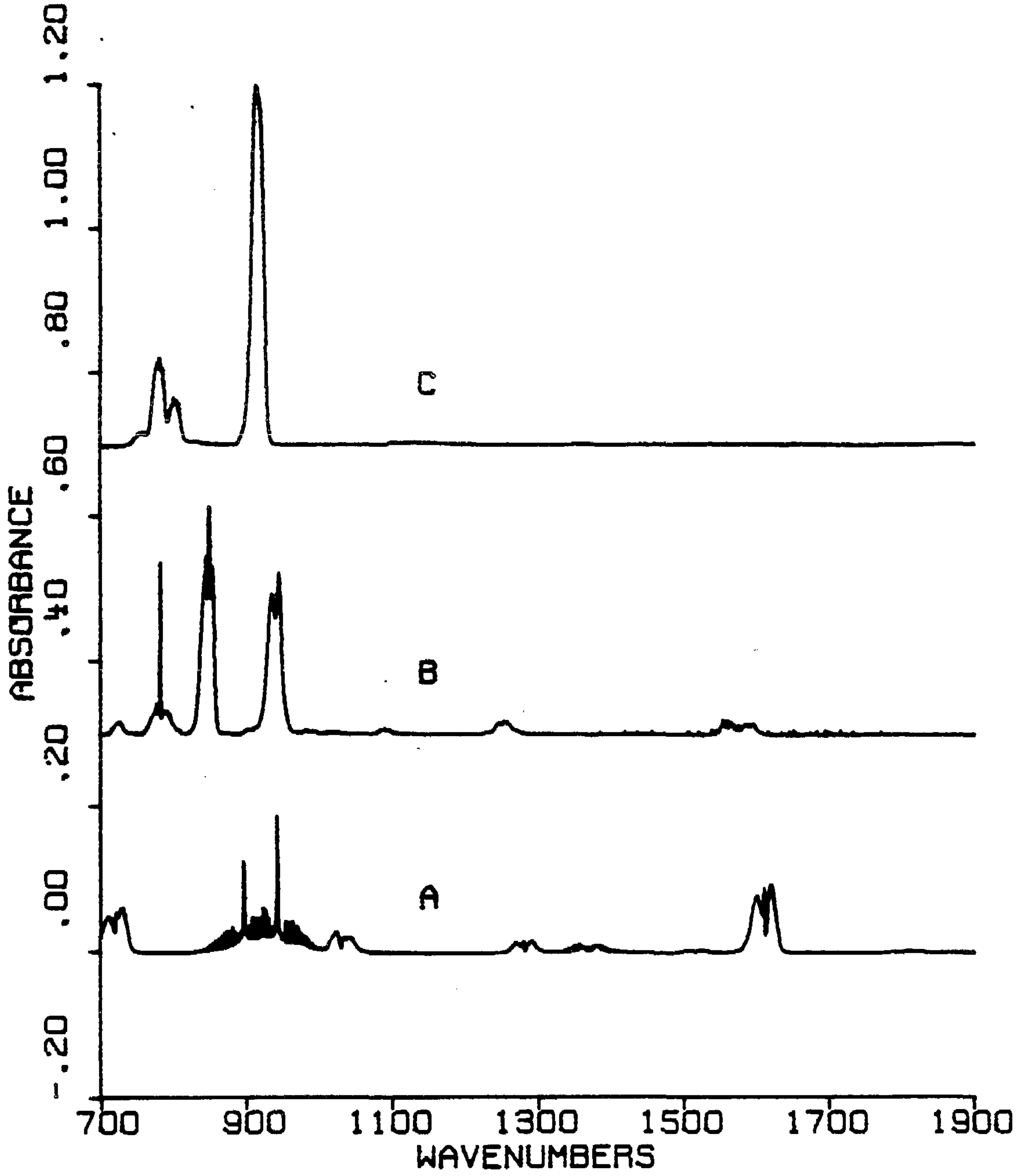


Figure III-1. FT-IR spectra of 5 ppm each of vinyl chloride (A), trichloroethene (B), and tetrachloroethene (C) at 62.9 m pathlength and 1 cm^{-1} resolution.

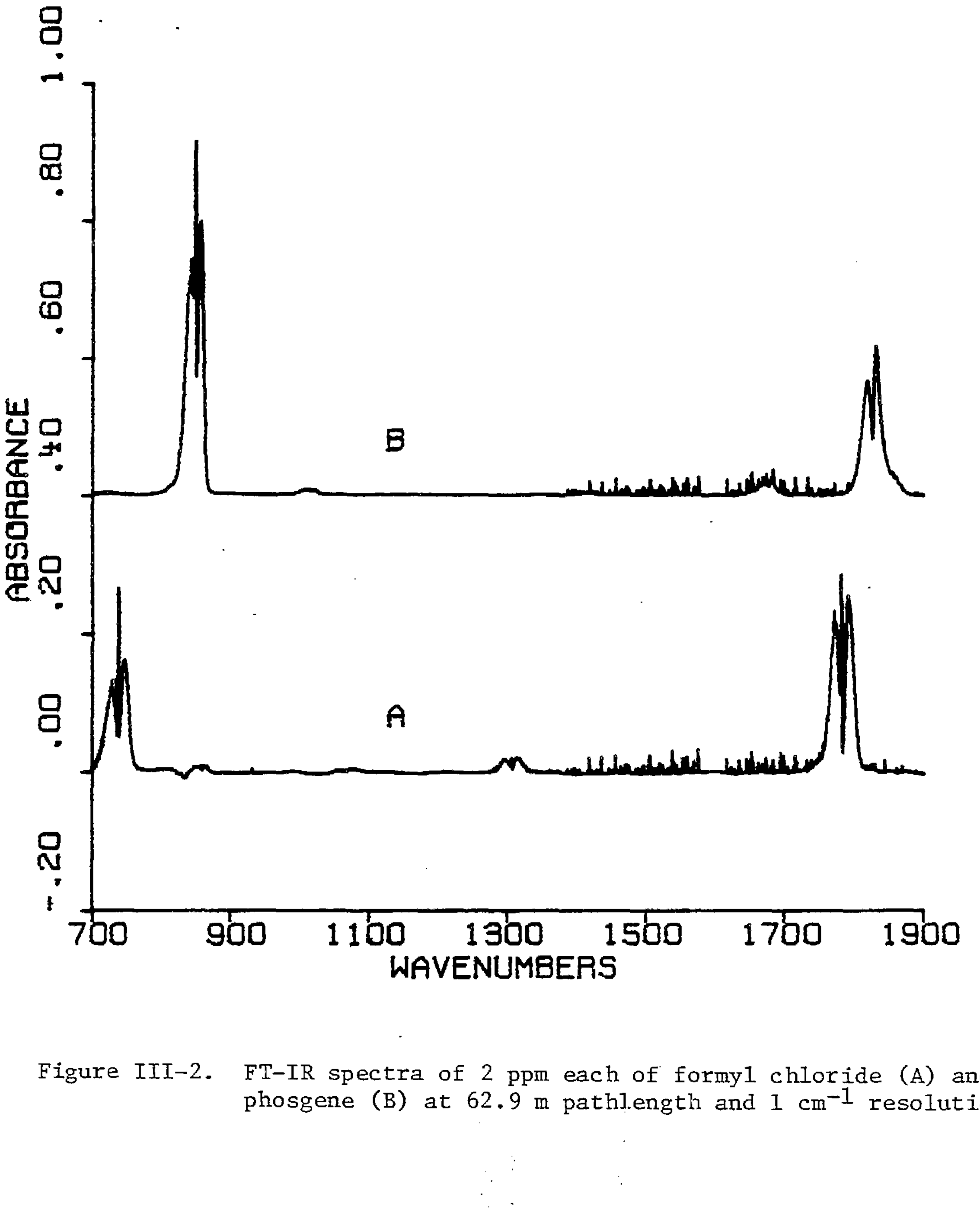


Figure III-2. FT-IR spectra of 2 ppm each of formyl chloride (A) and phosgene (B) at 62.9 m pathlength and 1 cm^{-1} resolution.

Table III-1. Experimental Conditions and Data for the Photolysis of CH_3ONO-NO-Vinyl Chloride-Air Mixtures at 298 K and Atmospheric Pressure

	Initial Concentrations (ppm)				HC(O)Cl	
Chamber	CH_3ONO	NO	Vinyl Chloride	$-\Delta$[Vinyl Chloride] (ppm)	(ppm)	Obs. Yield (%)
3700-ℓ all-Teflon	12	8	12.53	2.06	1.85	90
				3.33	2.79	84
				4.21	3.25	77
				4.77	3.52	74
5800-ℓ evacuable	10	5	9.64	1.09	1.00	92
				2.01	1.74	87
				2.53	2.10	83
				2.87	2.32	81

Table III-2. Experimental Conditions and Data for the Photolysis of CH_3ONO-NO-Trichloroethene-Air Mixtures at 298 K and Atmospheric Pressure

	Initial Concentrations (ppm)				HC(O)Cl		$COCl_2$	
Chamber	CH_3ONO	NO	Trichloroethene	-Δ[Trichloroethene] (ppm)	(ppm)	Obs. Yield (%)	(ppm)	Obs. Yield (%)
3700-ℓ all-Teflon	11	11	8.87	1.23	0.25	20	0.28	23
				2.16	0.40	19	0.44	20
				2.71	0.46	17	0.60	22
				3.18	0.52	16	0.74	23
				3.51	0.57	16	0.88	25
				3.69	0.59	16	0.98	27
5800-ℓ evacuable	10	5	10.21	2.71	0.57	21	0.67	25
				3.53	0.69	20	0.91	26
				4.01	0.76	19	1.06	26
				4.40	0.80	18	1.22	28
				4.71	0.84	18	1.32	28
				4.87	0.84	18	1.38	28
				5.10	0.85	17	1.48	29

Table III-3. Experimental Conditions and Data for the Photolysis of CH_3ONO-NO-Tetrachloroethene-Air Mixtures at 298 K and Atmospheric Pressure

Chamber	Initial Concentrations (ppm)			−Δ[Tetrachloroethene] (ppm)	COCl	
	CH_3ONO	NO	Tetrachloroethene		(ppm)	Obs. Yield (%)
3700-ℓ all-Teflon	11	11	7.84	0.12	0.034	28
				0.31	0.072	23
				0.42	0.11	26
				0.53	0.11	21
				0.60	0.13	22
				0.74	0.16	22
				0.81	0.17	21
				0.85	0.18	21
5800-ℓ evacuable	10	5	7.64	0.26	0.15	58
				0.52	0.24	46
				0.73	0.29	40
				1.03	0.35	34
				1.29	0.42	33
5800-ℓ evacuable	10	5	9.68	0.38	0.15	39
				0.65	0.25	38
				0.88	0.33	38
				1.05	0.36	34
				1.30	0.42	32
				1.47	0.47	32
				1.71	0.51	30
5800-ℓ evacuable	10	6	6.31[a]	0.16	0.083	52
				0.25	0.12	48
				0.37	0.15	41
				0.43	0.17	40
				0.48	0.19	40
				0.60	0.23	38
				0.85	0.25	29

[a] The pre-irradiation dark decay of tetrachloroethene was ≲1.3% over a 30 min time period.

formyl chloride (HC(O)Cl) from vinyl chloride, formyl chloride and phosgene ($COCl_2$) from trichloroethene, and phosgene from tetrachloroethene.

The yields of these products in Tables III-1 to III-3 have not been corrected for their loss due to reaction with OH radicals, photolysis, decomposition or wall reaction since the relevant data were not available for these loss processes. For these two products, formyl chloride is expected to photolyze, decompose and react with OH radicals, while the major loss process for phosgene under these experimental conditions is expected to be via wall decay. The occurrence of such loss processes can be seen from the decrease in the yields of formyl chloride during the CH_3ONO-NO-air irradiations of vinyl chloride and trichloroethene, and of $COCl_2$ during the CH_3ONO-NO-air photooxidation of tetrachloroethene (which had significantly longer irradiation times than did the trichloroethene system).

The formation yields of formyl chloride and phosgene can be obtained with reasonable accuracy from the data given in Tables III-1 to III-3 by extrapolating the observed formyl chloride and phosgene yields to zero reactive loss of the chloroethenes. These extrapolated yields, obtained by least squares analyses of the data in Tables III-1 to III-3, are as follows:

1. Vinyl chloride

Formyl chloride yield = 103 ± 4% and 99 ± 2% from the two runs (where the errors are two least squares standard deviations. Thus the yield of formyl chloride from the reaction of OH radicals with vinyl chloride is unity within the experimental errors.

2. Trichloroethene

Extrapolation of the formyl chloride yields to zero reaction gave formation yields of 22 ± 2% and 25 ± 2% for the two irradiations, respectively. The phosgene data gave extrapolated yields of 19 ± 6% and 20 ± 3%, respectively. Thus the yields of formyl chloride and phosgene from trichloroethene are approximately 24% and 20%, respectively and are identical within the experimental error limits.

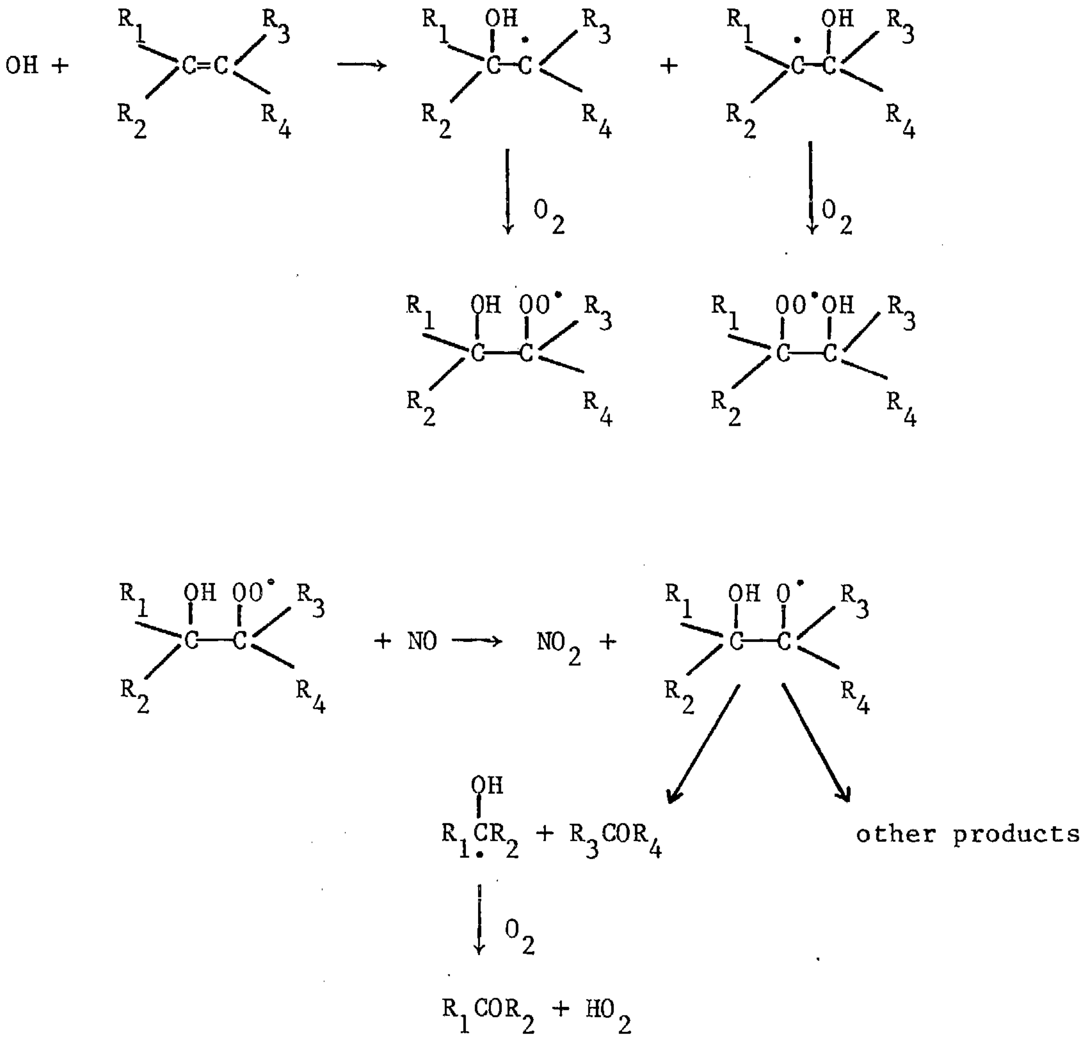
3. Tetrachloroethene

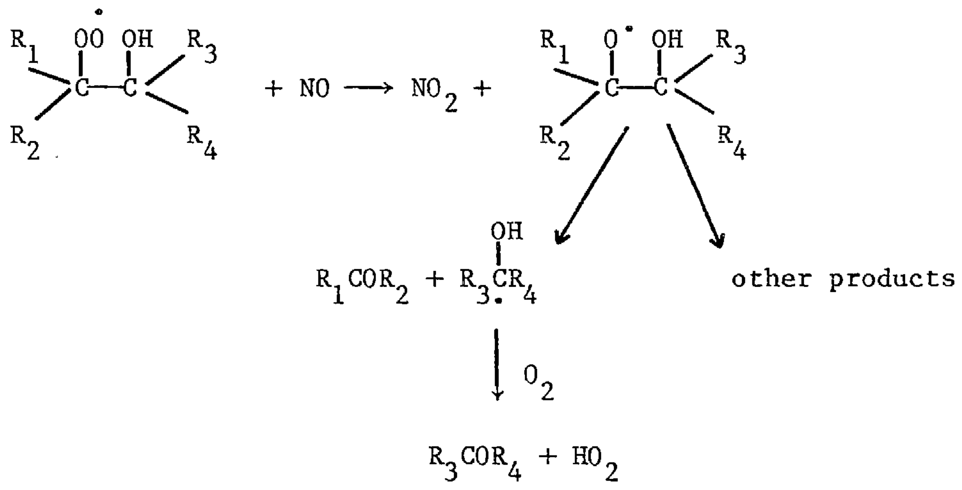
The phosgene yields extrapolated to zero reaction are 28 ± 3%, 61 ± 8%, 43 ± 3% and 55 ± 4%, respectively. Obviously the individual irradiations show considerable scatter, with that carried out in the 3700-ℓ all-Teflon chamber having an anomalously low yield. From the data in the 5800-ℓ evacuable chamber the phosgene yield from tetrachloroethene appears to be ~53%.

C. Discussion

The data obtained in this study allow the reaction pathways occurring in the reaction of OH radicals with the chloroethenes vinyl chloride, trichloroethene and tetrachloroethene to be quantified.

Based upon our present knowledge of the reactions of OH radicals with the haloalkenes (Atkinson et al. 1979) and the alkenes (Atkinson et al. 1979, Atkinson and Lloyd 1984), the reactions are expected to proceed via:





Hence if decomposition of the alkoxy radicals is their only loss process, then these chloroethenes would in essence be cleaved across the double bond to yield carbonyl compounds: formaldehyde and formyl chloride from vinyl chloride; formyl chloride and phosgene from trichloroethene; and phosgene from tetrachloroethene.

Our observed unit yield of formyl chloride from vinyl chloride implies a corresponding unit yield of formaldehyde, and shows that the reaction of OH radicals with vinyl chloride proceeds via essentially 100% cleavage of the double bond:

$$\mathrm{OH} + \mathrm{CH_2{=}CHCl} \xrightarrow[\downarrow\ \mathrm{NO_2}]{\mathrm{O_2,\ NO}} \mathrm{HCHO} + \mathrm{HC(O)Cl} + \mathrm{HO_2}$$

However, for trichloroethene, the yields of formyl chloride and phosgene, though essentially identical, are only ~20-25%. Hence it is evident that the reaction of OH radicals with trichloroethene leads, ~75-80% of the time, to products other than these cleavage products observed. An analogous situation occurs in the case of tetrachloroethene, where the observed ~53% yield of $COCl_2$ shows that the above discussed reaction scheme leaving to cleavage of the double bond occurs only ~25% of the time, with other unidentified products being formed in the majority of the reaction.

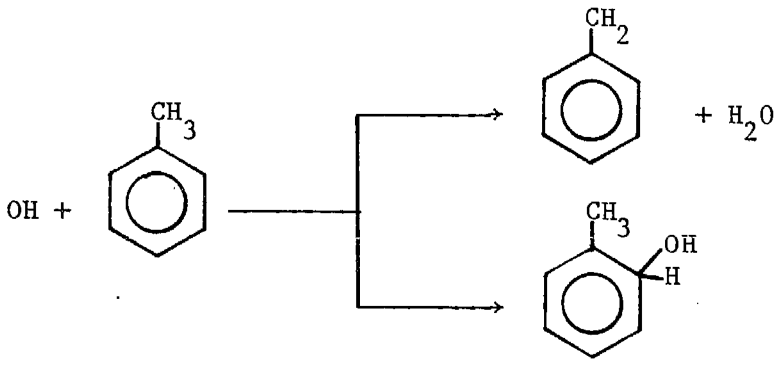
It should be noted that in both of the environmental chambers employed in this study, tetrachloroethene reacted only very slowly (significantly slower than did trichloroethene and vinyl chloride), consistent with its low OH radical rate constant.

IV. YIELDS OF GLYOXAL AND METHYLGLYOXAL FROM THE NO_x-AIR PHOTOOXIDATIONS OF TOLUENE AND m- AND p-XYLENE, AROMATIC CONSTITUENTS OF UNLEADED FUELS

A. Introduction

Aromatic hydrocarbons are important constituents of gasoline (Black et al. 1980, Carter et al. 1981) and other commercial fuels (Carter et al. 1981), with gasoline having an aromatic content of ~25-45% (Black et al. 1980). Black et al. (1980) have shown that the aromatic content of the total (tailpipe plus evaporative) hydrocarbon emissions from light duty motor vehicles is in the range of 10-30%. Thus a complete knowledge of the atmospheric chemistry of the aromatic hydrocarbons is necessary to assess the impacts on photochemical air pollution of their emissions into the atmosphere. However, despite numerous kinetic, product, mechanistic and computer modeling studies, the reaction pathways involved in the NO_x-air photooxidations of the aromatic hydrocarbons are still incompletely understood (Atkinson et al. 1980, Killus and Whitten 1982, Leone and Seinfeld 1984, Atkinson and Lloyd 1984).

Kinetic and environmental chamber studies have shown that under atmospheric conditions the sole loss process of the aromatic hydrocarbons is due to reaction with the hydroxyl radical (Atkinson et al. 1979, 1980, Atkinson and Lloyd 1984). These OH radical reactions have been shown to proceed via two pathways, namely H-atom abstraction from the substituent alkyl groups and OH radical addition to the aromatic ring (Atkinson et al. 1979, 1983c, Perry et al. 1977b, Kenley et al. 1981, Tully et al. 1981, Nicovich et al. 1981, Atkinson and Lloyd 1984) (taking toluene as an example)

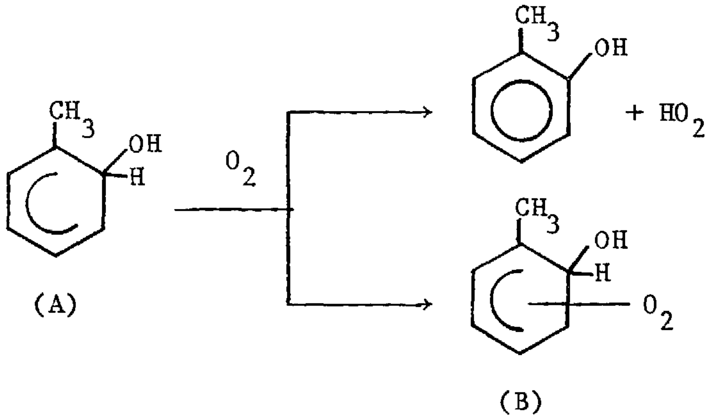


(1)

(2)

(A)

The H-atom abstraction route is relatively minor, accounting for ~8% of the overall reaction for toluene (Atkinson et al. 1983c) and ~2-4% for the xylenes and trimethylbenzenes (Perry et al. 1977b, Kenley et al. 1981, Nicovich et al. 1981). While the subsequent chemistry of the benzyl and substituted benzyl radicals appears to be adequately understood (Atkinson et al. 1980, Atkinon and Lloyd 1984), the subsequent chemistry of the OH-aromatic adducts is still not well established (Atkinson and Lloyd 1984). It has been proposed that the OH-aromatic adduct (A) can react with O_2 by two routes (Atkinson et al. 1980, Killus and Whitten 1982, Atkinson and Lloyd 1984)



(3)

(4)

For toluene the yield of o-cresol has been determined to be 13 ± 7% (Atkinson et al. 1983c) and, when combined with the (o-cresol/total cresol) formation ratio of ~0.8 (Kenley et al. 1981), this leads to a total isomeric cresol yield of ~16 ± 8%. For the remaining aromatic hydrocarbons the phenolic yields are not presently known.

The pathway involving O_2 addition to the OH-aromatic adducts to form the OH-aromatic-O_2 adducts (B) [reaction (4)] and subsequent reactions have been discussed in detail by Atkinson et al. (1980), Killus and Whitten (1982), and Atkinson and Lloyd (1984). Although the reaction sequences proposed are speculative, the α-dicarbonyls glyoxal, methylglyoxal and biacetyl have been identified and measured from o-xylene (Darnall et al. 1979, Takagi et al. 1980, Bandow et al. 1983, Atkinson et al. 1983c) and other aromatic hydrocarbons (Bandow et al. 1983). However, only for the formation of biacetyl from o-xylene has more than one study been carried out. In the most recent study, Bandow et al. (1983) have used long pathlength Fourier transform infrared (FT-IR) absorption spectroscopy to determine the yields of the α-dicarbonyls glyoxal, methylglyoxal and biacetyl from benzene, toluene, the xylenes and the trimethylbenzenes.

In this work we have used long pathlength FT-IR absorption spectroscopy and long pathlength differential optical absorption spectroscopy to determine the yields of glyoxal and methylglyoxal from the NO_x-air photooxidations of toluene, m-xylene and p-xylene at ~740 torr of air and 298 ± 2 K.

B. Experimental

The NO_x-air photooxidations of toluene, m-xylene and p-xylene were carried out in the SAPRC 5800-ℓ evacuable, Teflon-coated environmental chamber, with radiation being provided by a 25 KW Xenon arc (Winer et al. 1980). This chamber was equipped with two sets of multiple-reflection White-type optical systems (Figure IV-1). One set of these multiple-reflection optics, with a base path of 1.30 m, was interfaced to an FT-IR spectrometer. The second set, with a base path of 3.77 m, was interfaced to a differential optical absorption spectrometer (DOAS), as described previously (Plum et al. 1983).

DOAS measurements were carried out using pathlengths from 45.2 m to 150.8 m. The absorption spectra of glyoxal and methylglyoxal in the wavelength region ~250-470 nm are shown in Figure IV-2. Glyoxal was monitored in the wavelength region 430-460 nm, as described previously (Plum et al. 1983), with an optimum detection sensitivity of ~5 x 10^{11} molecule cm^{-3} for the maximum pathlength used (150.8 m). Methylglyoxal could also be monitored by DOAS in the same wavelength region, but due to its significantly lower differential absorption cross-section the optimum detection sensitivity at the maximum pathlength used (150.8 m) was ~5 x 10^{12} molecule cm^{-3}. However, at the shorter pathlengths used during the irradiations and in the presence of significant concentrations of NO_2, the unambiguous detection and measurement of methylglyoxal with the DOAS system during these experiments could not be carried out.

Glyoxal, methylglyoxal and the aromatic hydrocarbons were monitored by FT-IR absorption spectroscopy simultaneously with the DOAS measurements of glyoxal. For the FT-IR measurements, a pathlength of 62.9 m was routinely used with a spectral resolution (unapodized) of 1 cm^{-1} (optical

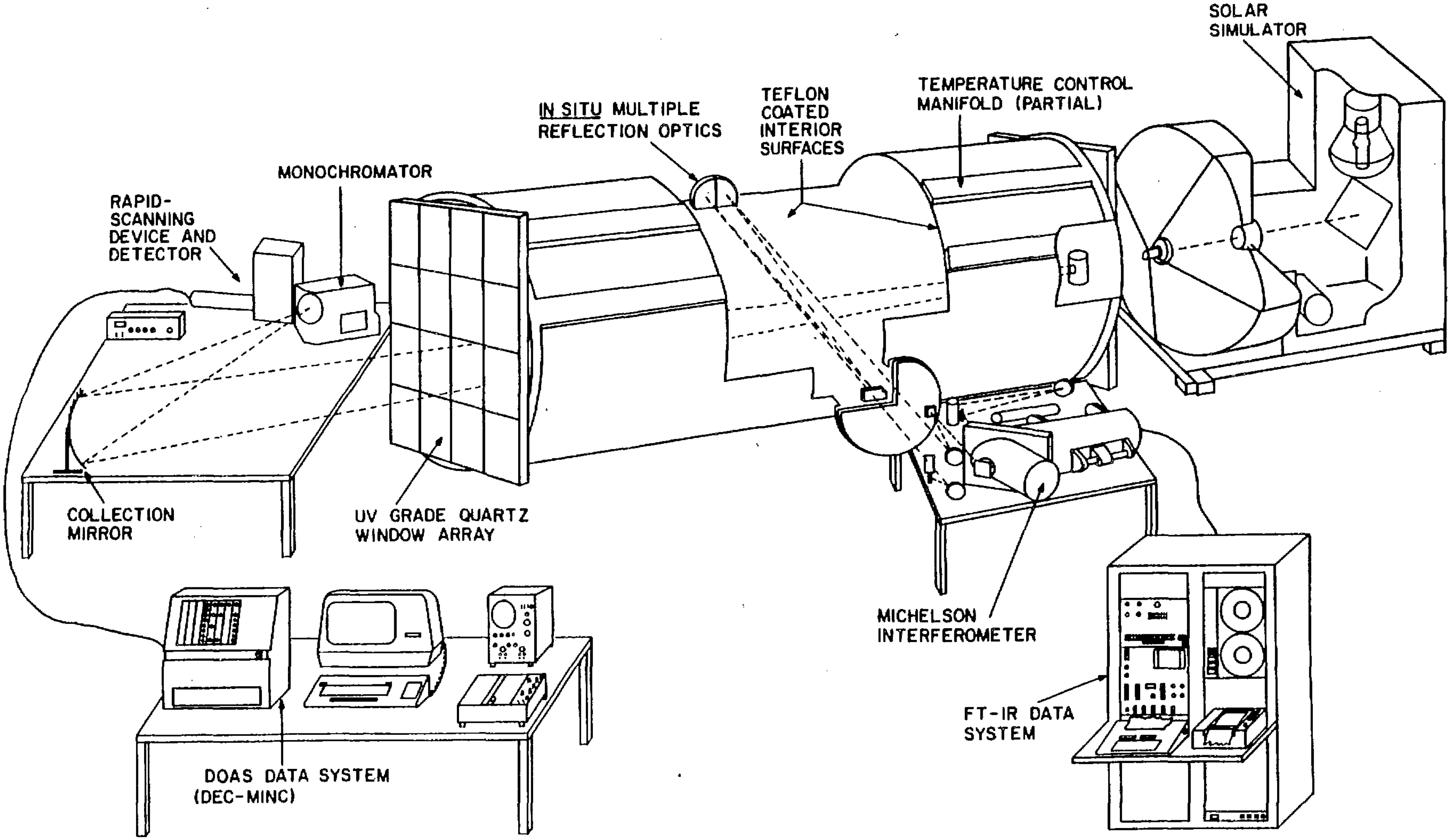


Figure IV-1. SAPRC evacuable chamber with *in situ* DOAS optics.

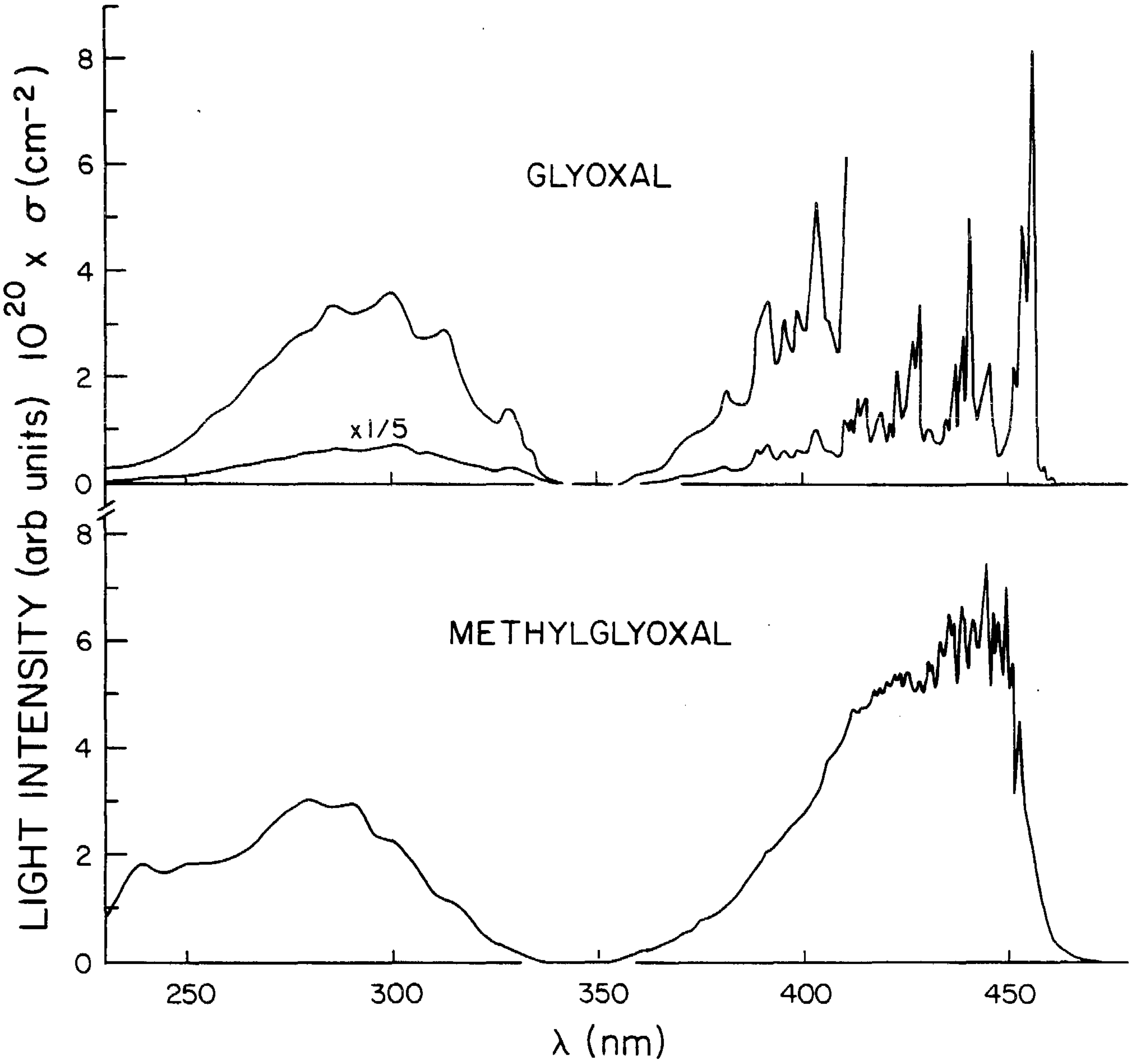


Figure IV-2. Absorption spectra of glyoxal and methylglyoxal in the wavelength region 250-470 nm.

path difference = 1 cm). Glyoxal and methylglyoxal were monitored at their absorptions at ~2830 cm^{-1} (Figure IV-3). Analyses of these superimposed bands were carried out using standard spectra recorded from authentic samples. The first step in these analyses involved the subtraction of the more highly structured band of glyoxal, as verified by the DOAS data (where applicable), followed by the determination of the residual absorption of methylglyoxal. FT-IR detection sensitivities for glyoxal and methylglyoxal were similar, being ~4 x 10^{12} molecule cm^{-3} at the pathlength and resolution employed.

Hydroxyl radicals were generated by the photolysis of methyl nitrite in air at wavelengths $\gtrsim$300 nm (Atkinson and Lloyd 1984)

$$CH_3ONO + h\nu \rightarrow CH_3O + NO$$

$$CH_3O + O_2 \rightarrow HCHO + HO_2$$

$$HO_2 + NO \rightarrow OH + NO_2$$

NO was included in the reaction mixtures in order to minimize the formation of O_3 and of NO_3 radicals. The initial concentrations of the CH_3ONO-NO-aromatic hydrocarbon-air mixtures were: CH_3ONO 10 ppm, NO 5 ppm, aromatic hydrocarbon 15-50 ppm; with one atmosphere (~740 torr) of synthetic air (80% N_2 + 20% O_2) as the diluent gas.

The light intensity in these experiments corresponded to a rate of photolysis of NO_2 in N_2 of 2.22 x 10^{-3} sec^{-1}, and to a biacetyl photolysis rate of (7.47 ± 0.21) x 10^{-5} sec^{-1} as determined from an irradiation of a biacetyl-air mixture, with analyses of biacetyl by gas chromatography (Plum et al. 1983).

C. Results

CH_3ONO-NO-air irradiations of toluene, m-xylene and p-xylene were carried out at 296 K and ~740 torr total pressure of air with irradiation times of up to 63 mins. The concentrations of the aromatic hydrocarbons, glyoxal and methylglyoxal were monitored by the FT-IR and/or DOAS techniques during these irradiations, and the resulting data are given in

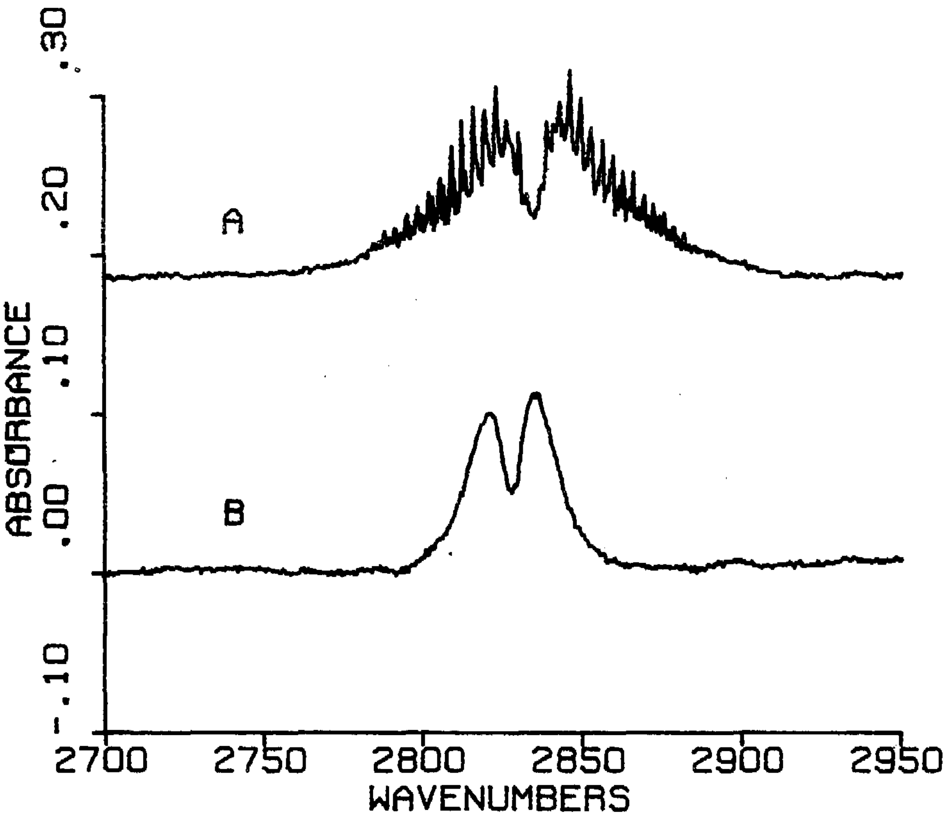


Figure IV-3. Infrared measurement bands of glyoxal (A) and methylglyoxal (B). Concentration = 5 ppm of each compound; pathlength = 62.9 m; resolution = 1 cm^{-1}.

Tables IV-1 to IV-3. For toluene and p-xylene, the glyoxal concentrations were determined by DOAS, with the methylglyoxal concentrations then being determined by FT-IR spectroscopy (see above). In the case of m-xylene both of the individual α-dicarbonyl yields were determined by FT-IR spectroscopy.

The observed α-dicarbonyl yields had to be corrected for reaction with OH radicals and photolysis (Plum et al. 1983) in order to derive the formation yields of these compounds. Since the reaction sequence is

$$\text{OH} + \text{aromatic} \xrightarrow{\text{NO, O}_2} \text{Y } \alpha\text{-dicarbonyl} \qquad (5)$$

$$\text{OH} + \alpha\text{-dicarbonyl} \rightarrow \text{products} \qquad (6)$$

$$\alpha\text{-dicarbonyl} + h\nu \rightarrow \text{products} \qquad (7)$$

where the complex reaction (5) includes reactions (1)-(4) discussed above, and Y is the formation yield of the individual α-dicarbonyls. Making the reasonable assumption that the OH radical concentrations were essentially constant over the small irradiation periods between the FT-IR and DOAS measurements, then from the measured aromatic hydrocarbon decays,

$$[\text{OH}] = \frac{1}{k_5(t_2-t_1)} \ln \left\{ \frac{[\text{aromatic}]_{t_1}}{[\text{aromatic}]_{t_2}} \right\} \qquad (\text{I})$$

where [OH] is the average OH radical concentration over the time period t_1 to t_2, k_5 is the rate constant for reaction (5) [where $k_5 = k_1 + k_2$], and $[\text{aromatic}]_{t_1}$ and $[\text{aromatic}]_{t_2}$ are the aromatic hydrocarbon concentrations at times t_1 and t_2, respectively.

Furthermore,

$$[\alpha\text{-dicarbonyl}]_{t_2} = [\alpha\text{-dicarbonyl}]_{t_1} \left[e^{-(k_6[\text{OH}] + k_7)(t_2-t_1)} \right]$$

$$+ \frac{Y_{t_1-t_2}[\text{aromatic}]_{t_1} k_5[\text{OH}]}{[(k_6-k_5)\ [\text{OH}] + k_7]} \left[e^{-k_5[\text{OH}](t_2-t_1)} - e^{-(k_6[\text{OH}] + k_7)(t_2-t_1)} \right] \qquad (\text{II})$$

Table IV-1. Experimental Data for the Formation of Glyoxal and Methylglyoxal from the CH_3ONO-NO-Air Photooxidations of Toluene

EC	10^{-14} x Initial Concentrations (molecule cm^{-3})			10^{-13} x $-\Delta$[Toluene]	10^{-13} x [Glyoxal][a] (molecule cm^{-3})		10^{-13} x [Methylglyoxal][b] (molecule cm^{-3})	
Run No.	CH_3ONO	NO	Toluene	(molecule cm^{-3})	Obs.	Corr[c]	Obs.	Corr[c]
934	2.80	1.41	13.42	2.66	0.65	0.66	0.41	0.42
				6.53	1.34	1.42	0.84	0.92
				10.30	1.68	1.85	1.01	1.19
				12.12	2.09	2.33	1.08	1.32
941	3.38	1.13	5.07	3.19	0.67	0.71	0.41	0.45
				5.04	0.94	1.04	0.55	0.65
				6.38	0.84	1.00	0.70	0.85
				7.49	0.98	1.19	0.55	0.76
				8.54	1.15	1.41	0.74	1.00

---

[a] Determined by DOAS.
[b] Determined by FT-IR spectroscopy.
[c] Corrected for photolysis and reaction with OH radicals (see text).

Table IV-2. Experimental Data for the Formation of Glyoxal and Methylglyoxal from the CH_3ONO-NO-Air Photooxidations of m-Xylene

EC Run No.	10^{-14} x Initial Concentrations (molecule cm^{-3})			10^{-13} x $-\Delta$[m-xylene] (molecule cm^{-3})	10^{-13} x [Glyoxal][a] (molecule cm^{-3})		10^{-13} x [Methylglyoxal][a] (molecule cm^{-3})	
	CH_3ONO	NO	m-Xylene		Obs.	Corr[b]	Obs.	Corr[b]
939	3.40	1.13	4.21	7.25	0.65	0.68	1.27	1.38
				9.94	1.03	1.10	1.78	2.00
				12.10	0.84	0.95	2.42	2.78
				14.26	1.13	1.28	2.78	3.32
				15.74	1.34	1.53	3.34	4.03
				17.02	1.66	1.89	3.36	4.21
				18.24	1.63	1.92	3.41	4.42
940	3.39	1.13	4.38	6.84			1.61	1.73
				9.14			2.23	2.48
				10.99			2.83	3.26
				12.74			2.66	3.24
				14.40			2.90	3.65
				16.25			3.84	4.79
				17.86			3.55	4.72

---

[a] Determined by FT-IR spectroscopy.

[b] Corrected for photolysis and reaction with OH radicals (see text).

Table IV-3. Experimental Data for the Formation of Glyoxal and Methylglyoxal from the CH_3ONO-NO-Air Photooxidations of p-Xylene

EC	10^{-14} x Initial Concentrations (molecule cm^{-3})			10^{-13} x $-\Delta$[p-Xylene]	10^{-13} x [Glyoxal][a] (molecule cm^{-3})		10^{-13} x [Methylglyoxal][b] (molecule cm^{-3})	
Run No.	CH_3ONO	NO	p-Xylene	(molecule cm^{-3})	Obs.	Corr[c]	Obs.	Corr[c]
938	3.38	1.13	4.71	4.90	1.63	1.72	1.08	1.16
				7.54	2.04	2.23	1.39	1.59
				9.48	2.35	2.65	1.49	1.80
				11.47	2.62	3.04	1.54	1.97
				13.37	2.78	3.34	1.99	2.58
				15.65	2.81	3.54	2.30	3.11
				17.47	3.05	3.95	2.14	3.13
				18.07	2.78	3.75	2.02	3.10
937	3.08	1.17	3.85	16.25	2.86	3.71	2.16	3.27

[a] Determined by DOAS.
[b] Determined by FT-IR spectroscopy.
[c] Corrected for photolysis and reaction with OH radicals (see text).

where $[\alpha\text{-dicarbonyl}]_{t_1}$ and $[\alpha\text{-dicarbonyl}]_{t_2}$ are the α-dicarbonyl concentrations observed at times t_1 and t_2, respectively, and $Y_{t_1-t_2}$ is the observed yield of the individual α-dicarbonyls over the time period t_1 to t_2.

From equations (I) and (II) the corrected α-dicarbonyl yields are given by:

$$[\alpha\text{-dicarbonyl}]_{t_2}^{corr} = [\alpha\text{-dicarbonyl}]_{t_1}^{corr} + Y_{t_1-t_2}([\text{aromatic}]_{t_2} - [\text{aromatic}]_{t_1}) \qquad \text{(III)}$$

where $[\alpha\text{-dicarbonyl}]_{t_1}^{corr}$ and $[\alpha\text{-dicarbonyl}]_{t_2}^{corr}$ are the α-dicarbonyl concentrations at times t_1 and t_2, respectively, after correction for reaction with OH radicals and photolysis.

Rate constants k_5 and k_6 were taken from the literature (Plum et al. 1983, Atkinson and Lloyd 1984). Values of k_7 were obtained by ratioing the previously determined photolysis rates for glyoxal, methylglyoxal, biacetyl and NO_2 (Plum et al. 1983) with the presently determined photolysis rates of NO_2 and biacetyl, yielding values of k_7 for these experimental conditions of 1.66×10^{-5} sec^{-1} and 4.0×10^{-5} sec^{-1} for glyoxal and methylglyoxal, respectively. Use of these rate data together with equations (I)-(III) allowed the observed concentrations of glyoxal and methylglyoxal to be corrected for photolysis and reaction with OH radicals. The correction factors, $[\alpha\text{-dicarbonyl}]_t^{corr}/[\alpha\text{-dicarbonyl}]_t$, were in all cases ≤ 1.35 for glyoxal and ≤ 1.54 for methylglyoxal.

The experimental data are given in Tables IV-1 to IV-3, together with the corrected values derived from equations (I)-(III). These corrected α-dicarbonyl concentrations, $[\alpha\text{-dicarbonyl}]_t^{corr}$, are plotted against the amounts of aromatic hydrocarbon consumed, $-\Delta[\text{aromatic}]$ [i.e., $([\text{aromatic}]_t - [\text{aromatic}]_{t_o})$] according to equation (III) in Figure IV-4, and the yields, Y, of glyoxal and methylglyoxal derived from least squares analyses of these data are listed in Table IV-4.

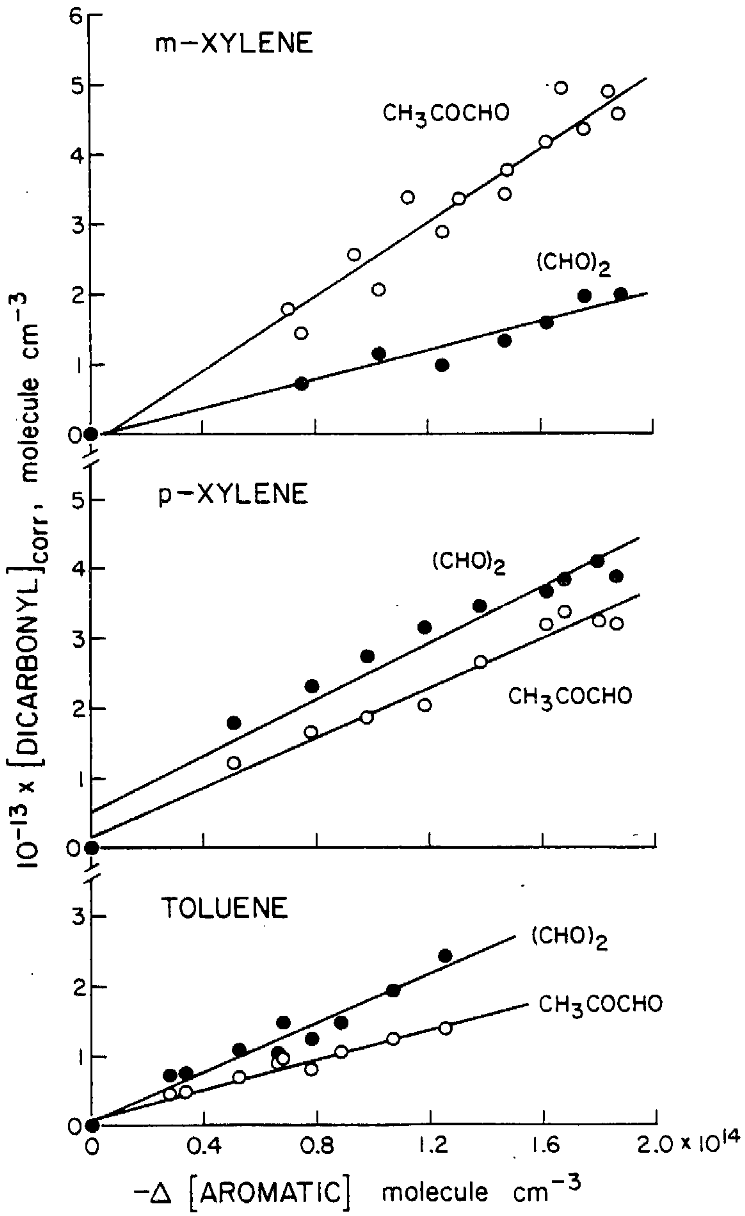


Figure IV-4. Plot of the glyoxal and methylglyoxal concentrations, corrected for reaction with OH radicals and photolysis (see text), against the amount of the aromatic hydrocarbon consumed, for the CH_3ONO-NO-air irradiations of toluene, m-xylene and p-xylene.

Table IV-4. Glyoxal and Methylglyoxal Yields from the CH_3ONO-NO-Air Photooxidations of Toluene, m-Xylene and p-Xylene at Room Temperature, and Atmospheric Pressure, Together with the Data of Bandow et al. (1983)

	Yield[a]			
	Glyoxal		Methylglyoxal	
Aromatic Hydrocarbon	This work	Bandow et al. (1983)	This work	Bandow et al. (1983)
Toluene	0.173 ± 0.029	0.15 ± 0.04	0.105 ± 0.016	0.14 ± 0.04
m-Xylene	0.104 ± 0.020	0.13 ± 0.03	0.265 ± 0.035	0.42 ± 0.05
p-Xylene	0.200 ± 0.032	0.24 ± 0.02	0.178 ± 0.021	0.12 ± 0.02

[a] The indicated errors are two least squares standard deviations.

D. Discussion

The glyoxal and methylglyoxal yields from toluene, m-xylene and p-xylene obtained in this work are compared in Table IV-4 with the yields recently reported by Bandow et al. (1983). It can be seen that the magnitude of these yields are in good agreement, with the only significant discrepancy being that for the methylglyoxal yield from m-xylene, where Bandow et al. (1983) obtained a value ~50% higher than the present work. Clearly, however, the present data and those of Bandow et al. (1983) define reasonably closely the yields of these α-dicarbonyls from the three aromatic hydrocarbons studied here.

For toluene the abstraction pathway [reaction (1)] has been shown to account for ~8% of the overall OH radical reaction (Atkinson et al. 1983c), and reaction (3) has been shown to account for ~16 ± 8% of the overall reaction (Atkinson et al. 1983c). Hence, the inclusion of reaction pathways resulting in the formation of ~28% of glyoxal and methylglyoxl [together with the corresponding co-products (Atkinson and Lloyd 1984)] still account for only ~50 (±15)% of the overall reaction pathways. Clearly the products and mechanisms of a major portion of the OH-aromatic reactions under atmospheric conditions are presently not identified.

The present data obviously have major implications for the validity and predictions of present chemical kinetic computer models of aromatic hydrocarbons, particularly those being employed in airshed models for the purpose of developing emission control strategies. Specifically, previous chemical computer models have assumed that the reactions subsequent to reaction (4) yield exclusively α-dicarbonyls (together with the corresponding co-products). However, the α-dicarbonyl yields determined in this study are too low to be explained by any existing chemical computer mechanism (Atkinson et al. 1980, 1982e, Killus and Whitten 1982, Leone and Seinfeld 1984). Hence all these existing chemical mechanisms are suspect, and their predictions under conditions removed from the environmental chamber data (against which these mechanisms were tested) may well be incorrect.

Obviously, further studies under atmospheric conditions are needed to identify the remaining products and reaction pathways involved following the initial OH radical reaction with the aromatic hydrocarbons. Only from such studies will realistic and accurate chemical models of these systems be developed.

V. FORMATION OF ALKYL NITRATES FROM THE REACTION OF BRANCHED AND CYCLIC ALKYL PEROXY RADICALS WITH NITRIC OXIDE: IMPLICATIONS TO THE ATMOSPHERIC CHEMISTRY OF FUELS FOR DIESEL AND GASOLINE ENGINES

A. Introduction and Background

Organic peroxy (RO_2) radicals are important intermediates involved in the degradation of organics emitted into the atmosphere (Finlayson-Pitts and Pitts 1977, Atkinson and Lloyd 1984), and until recently it has been assumed in airshed chemical computer models that their dominant reaction under polluted atmospheric conditions proceeds via reaction with NO to form NO_2 and an alkoxy radical (Finlayson-Pitts and Pitts 1977, Atkinson and Lloyd 1984).

$$RO_2 + NO \rightarrow RO + NO_2 \qquad (1)$$

However, studies in these laboratories have shown (Darnall et al. 1976, Atkinson et al. 1982a, 1983a) that for alkyl peroxy radicals the reaction with NO to form alkyl nitrates also occurs to a significant extent.

$$RO_2 + NO \xrightarrow{M} RONO_2 \qquad (2)$$

For the alkyl peroxy radicals generated from the C_2-C_8 n-alkanes, the fraction of the overall reaction forming $RONO_2$, $k_2/(k_1 + k_2)$, increases monotonically with the carbon number of the RO_2 radical from ≤ 0.014 for ethane to ~0.33 for n-octane at 299 K and 735 torr total pressure (Atkinson et al. 1982a). Furthermore, the alkyl nitrate yields from the n-pentane and n-heptane systems are temperature and pressure dependent, increasing with increasing pressure and with decreasing temperature (Atkinson et al. 1983a). However, apart from a study carried out by Takagi et al. (1981) dealing with the NO_x-air photooxidations of the C_5-C_7 cycloalkanes, previous investigations (Darnall et al. 1976, Atkinson et al. 1982a, 1983a) have dealt only with the peroxy radicals derived from the n-alkane series, and no data are available concerning the corresponding reactions of peroxy radicals formed from branched alkanes.

In this program, we have extended our previous studies (Atkinson et al. 1982a, 1983a) to investigate the formation of alkyl nitrates from the reactions of NO with alkyl peroxy radicals generated from the cyclic and branched alkanes neopentane, cyclohexane, 2-methylbutane, 2-methylpentane and 3-methylpentane at 298 ± 2 K and 735 torr total pressure. As an integral part of this work, rate constants for the reaction of OH radicals with several of the alkyl nitrates formed in these systems have also been determined at 298 ± 2 K.

B. Experimental

The experimental techniques used for the determination of OH radical rate constants for the alkyl nitrates and of the alkykl nitrate yields were as described below:

1. Determination of OH Radical Rate Constants

As described previously (Atkinson et al. 1982b,c), a relative rate technique was used. Hydroxyl radicals were generated by the photolysis, at wavelengths $\gtrsim 290$ nm, of methyl nitrite in air at part-per-million concentrations (1 ppm = 2.38×10^{13} molecule cm^{-3} at 298 K and 735 torr total pressure)

$$CH_3ONO + h\nu \rightarrow CH_3O + NO$$

$$CH_3O + O_2 \rightarrow HCHO + HO_2$$

$$HO_2 + NO \rightarrow OH + NO_2$$

In order to minimize the formation of O_3 during these irradiations, NO was added to the reaction mixtures, which had initial concentrations of CH_3ONO, 10-16 ppm; NO, ~5 ppm and ~1.0 ppm each of the reference alkane (n-butane for these experiments) and the alkyl nitrates. Ultra-zero air (Liquid Carbonic, <0.1 ppm hydrocarbons) was used as the diluent gas.

Irradiations were carried out in an ~60-ℓ FEP Teflon cylindrical reaction bag surrounded by 24 GE F15T8-BL 15-watt blacklights. By switching off sets of lamps, light intensities of one-third and two-thirds of the maximum could be obtained. Prior to irradiation, the reaction bag/lamp assembly was covered with an opaque cover to avoid any photolysis of the reactants.

n-Butane (the reference organic) and the alkyl nitrates were quantitatively monitored by gas chromatography with flame ionization detection

(GC-FID). n-Butane was analyzed using either a 20-ft x 0.125-in. stainless steel (SS) column with 5% DC703/C20M on 100/120 mesh AW, DMCS Chromosorb G, operated at 333 K, or a 36-ft x 0.125-in. SS column of 10% 2,4-dimethylsulfolane on C-22 Firebrick (60/80 mesh) operated at 273 K. The alkyl nitrates were analyzed using a 5-ft or 10-ft x 0.125-in. column of 5% or 10% Carbowax 600 on C-22 Firebrick (100/110 mesh) operated at 348 K. NO, NO_x and O_3 were monitored by chemiluminescence instruments. All irradiations were carried out at 298 ± 2 K and 735 torr total pressure.

2. Determination of Alkyl Nitrate Formation Yields

As in our previous studies (Atkinson et al. 1982a, 1983a), RO_2 radicals were formed in the presence of NO by photolysis of CH_3ONO-NO-alkane-air mixtures at $\gtrsim$290 nm

$$CH_3ONO + h\nu \rightarrow CH_3O + NO$$

$$CH_3O + O_2 \rightarrow HCHO + HO_2$$

$$HO_2 + NO \rightarrow OH + NO_2$$

$$OH + RH \rightarrow R^{\bullet} + H_2O$$

$$R + O_2 \xrightarrow{M} RO_2$$

with typical initial reactant concentrations of CH_3ONO, ~1 ppm; NO, ~1 ppm; and alkane, ~1 ppm. Irradiations were carried out in the ~60-ℓ Teflon cylindrical reaction bag at 298 ± 2 K and 735 torr total pressure, and the alkanes and the alkyl nitrates were quantitatively monitored prior to and during the irradiations by GC-FID using the columns described above.

3. Materials

Gas chromatographic (GC) calibrations and retention times for neopentyl nitrate, cyclohexyl nitrate, 3-nitro-2-methylbutane, 2-nitro-2-methylpentane and 2-nitro-3-methylpentane were determined using authentic samples obtained from Fluorochem, Inc. of Azusa, CA, (the 2-nitro-3-methylpentane was present as the two diastereomers, which were only partially resolved by GC-FID). The 2-nitro-2-methylpentane showed significant decomposition with time, so it was not used as a calibration standard, though it was sufficiently stable to be used in the kinetic studies. GC calibrations for 2-nitro-2-methylpentane and the 3- and 4-nitro-2-methylpentanes (which were not resolved in the GC analyses) were obtained by assuming that their GC-FID peak area responses were identical to that for their 2-nitro-3-methylpentane isomer.

Methyl nitrite was prepared as described previously (Atkinson et al. 1982c), and the alkanes n-butane, neopentane, cyclohexane, 2-methylbutane, 2-methylpentane and 3-methylpentane were obtained from commercial sources and used as received.

C. Results and Discussion

1. OH Radical Kinetics

Rate constants for the reaction of OH radicals with neopentyl nitrate, cyclohexyl nitrate, 3-nitro-2-methylbutane, 2-nitro-2-methylpentane and 2-nitro-3-methylpentane were determined, relative to that for the reaction of OH radicals with n-butane, from irradiations of a series of CH_3ONO-NO-alkyl nitrate-n-butane-air mixtures. In order to optimize the gas chromatographic analyses the following alkyl nitrate mixtures were used: neopentyl nitrate + cyclohexyl nitrate; 2-nitro-2-methylpentane; and 3-nitro-2-methylbutane + 2-nitro-3-methylpentane. For these mixtures, duplicate irradiations were carried out with differing initial concentrations of CH_3ONO.

In addition to reacting with CH_3ONO, NO, NO_2 and the organic reaction products, the OH radicals generated from the photolysis of CH_3ONO in air can react with the alkyl nitrates and with n-butane

$$\text{OH + alkyl nitrate} \rightarrow \text{products} \qquad (3)$$

$$\text{OH + n-butane} \rightarrow \text{products} \qquad (4)$$

Since n-butane and the alkyl nitrates are consumed essentially solely by reaction with OH radicals (Atkinson et al. 1982b,c), and since dilution due to sampling was avoided by use of a collapsible Teflon reaction bag, then in the absence of any wall adsorption (Atkinson et al. 1982b,c)

$$\frac{-d\ln[\text{alkyl nitrate}]}{dt} = k_3[\text{OH}] \qquad \text{(I)}$$

and

$$\frac{-d\ln[\text{n-butane}]}{dt} = k_4[\text{OH}] \qquad \text{(II)}$$

Hence

$$\ln\left\{\frac{[\text{alkyl nitrate}]_{t_o}}{[\text{alkyl nitrate}]_t}\right\} = k_3 \int_{t_o}^{t} [\text{OH}]dt \qquad \text{(III)}$$

$$\ln\left\{\frac{[\text{n-butane}]_{t_o}}{[\text{n-butane}]_t}\right\} = k_4 \int_{t_o}^{t} [\text{OH}]dt \qquad \text{(IV)}$$

and eliminating the OH radical concentration leads to

$$\ln\left\{\frac{[\text{alkyl nitrate}]_{t_o}}{[\text{alkyl nitrate}]_t}\right\} = \frac{k_3}{k_4} \ln\left\{\frac{[\text{n-butane}]_{t_o}}{[\text{n-butane}]_t}\right\} \qquad \text{(V)}$$

where $[\text{alkyl nitrate}]_{t_o}$ and $[\text{n-butane}]_{t_o}$ are the concentrations of the alkyl nitrate and n-butane, respectively, at time t_o, $[\text{alkyl nitrate}]_t$ and $[\text{n-butane}]_t$ are the corresponding concentrations at time t, and k_3 and k_4 are the rate constants for reactions (3) and (4), respectively.

Thus plots of $\ln([\text{alkyl nitrate}]_{t_o}/[\text{alkyl nitrate}]_t)$ against $\ln([\text{n-butane}]_{t_o}/[\text{n-butane}]_t)$ should yield straight lines with a zero intercept and a slope of k_3/k_4. Representative plots of equation (V) are shown in Figures V-1 and V-2, and the rate constant ratios k_3/k_4 obtained from such plots by least squares analyses are given in Table V-1. In all cases the least squares intercepts of such plots were within two standard deviations of zero.

The rate constant ratios k_3/k_4 given in Table V-1 can be placed on an absolute basis using a rate constant k_4 for the reaction of OH radicals with n-butane of 2.58×10^{-12} cm^3 molecule^{-1} sec^{-1} (Atkinson et al. 1982b), the mean of the absolute literature values of (in units of 10^{-12} cm^3 molecule^{-1} sec^{-1}) 2.57 (Griener 1970), 2.35 ± 0.35 (Stuhl 1973), 2.72

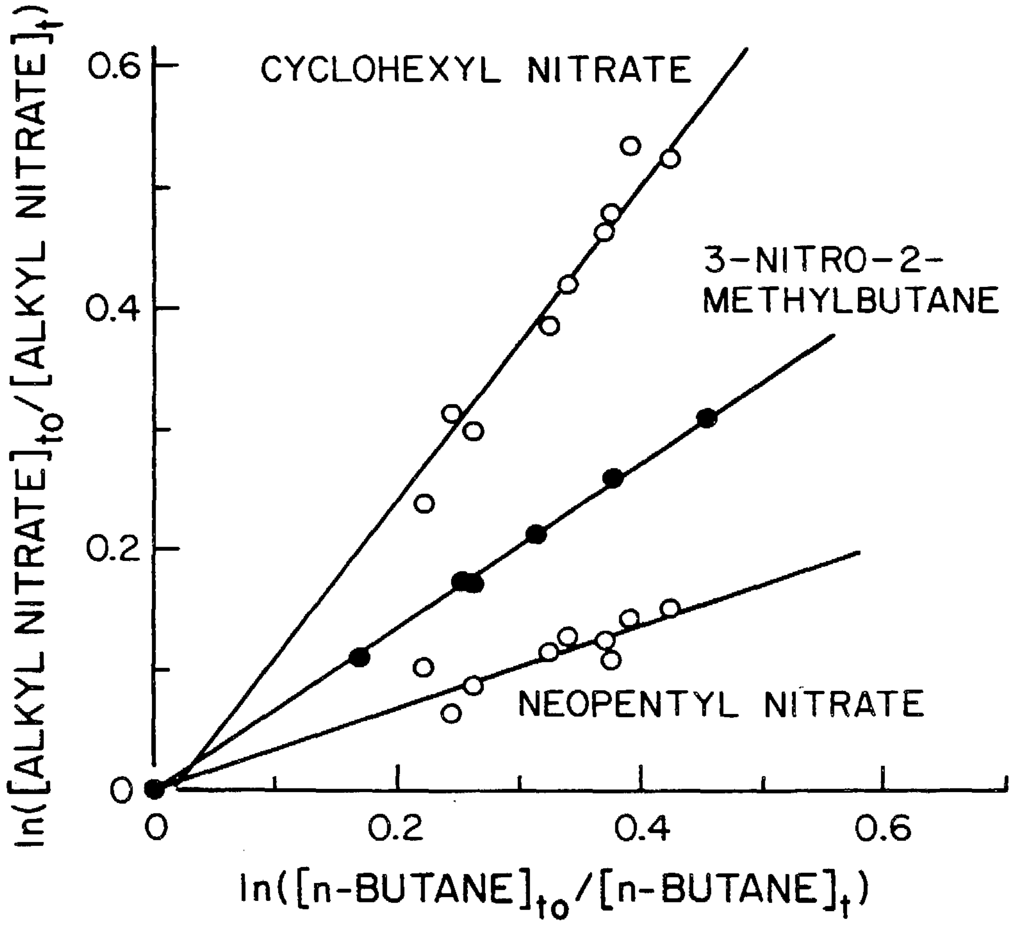


Figure V-1. Plot of equation (V) for cyclohexyl nitrate, 3-nitro-2-methylbutane and neopentyl nitrate.

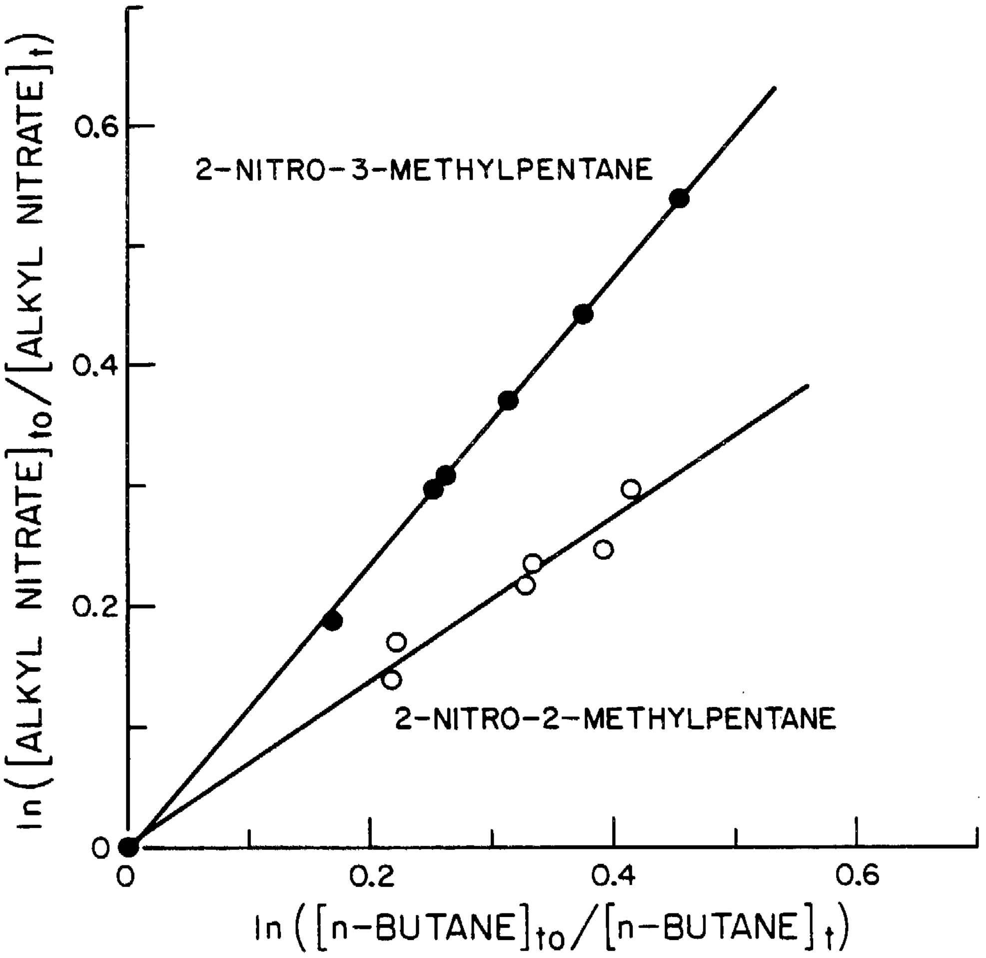


Figure V-2. Plot of equation (V) for 2-nitro-3-methylpentane and 2-nitro-2-methylpentane.

Table V-1. Rate Constant Ratios k_3/k_4 and Rate Constants k_3 for the Reaction of OH Radicals with a Series of Alkyl Nitrates at 298 ± 2 K

Alkyl nitrate	k_3/k_4[a]	$10^{12} \times k_3$ (cm^3 $molecule^{-1}$ sec^{-1})[a,b]
Neopentyl nitrate	0.336 ± 0.080	0.87 ± 0.21
Cyclohexyl nitrate	1.30 ± 0.14	3.35 ± 0.36
3-Nitro-2-methylbutane	0.679 ± 0.020	1.75 ± 0.06
2-Nitro-2-methylpentane	0.677 ± 0.085	1.75 ± 0.22
2-Nitro-3-methylpentane[c]	1.19 ± 0.03[c]	3.07 ± 0.08[c]

[a] Indicated error limits are two least squares standard deviations.

[b] Placed on an absolute basis using a rate constant, k_4, for the reaction of OH radicals with n-butane of 2.58×10^{-12} cm^3 $molecule^{-1}$ sec^{-1} (Atkinson et al. 1982b).

[c] 2-Nitro-3-methylpentane is present as the two diastereomers, with identical (within ~5%) OH radical rate constants (the individual rate constant ratios were 1.17 ± 0.03 and 1.20 ± 0.03). The values of k_3/k_4 and k_3 given are from a least squares analysis of the combined data for these two diastereomers.

± 0.27 (Perry et al. 1976), and 2.67 ± 0.22 (Paraskevopoulos and Nip 1980). The rate constants so derived, which are the first reported data for these alkyl nitrates, are also given in Table V-1. These rate constants show that, consistent with our previous data (Atkinson et al. 1982c), the presence of the nitrate group decreases the overall OH radical rate constant, compared to those for the parent alkanes, by up to a factor of ~3.3. It is also of interest to note that, as may be expected, the two diastereomers of 2-nitro-3-methylpentane have identical (within ~5%) OH radical rate constants.

Recently in studies of the kinetics of OH radical reactions with a series of alkanes we have shown that the overall rate constants can be estimated from the number of CH_3-, $-CH_2$-, and >CH- groups and the associated group rate constants, with the rate constant per $-CH_2$- and >CH- group depending on the identity of the neighboring groups (Atkinson et al. 1982d, 1984a). This group rate constant estimation technique can be extended to substituted alkanes such as alkyl nitrates (Atkinson et al. 1982b), and from our previous study of the kinetics of the reactions of OH radicals with a series of alkyl nitrates (Atkinson et al. 1982c) the following group rate constants (in units of 10^{-12} cm^3 molecule^{-1} sec^{-1}) were derived:

$$k[OH + CH_2ONO_2(CH_2)] \cong k[OH + CHONO_2(R)_2] \cong 0,$$

$$k[OH + CH_3(CHONO_2)] \cong 0.09,$$

and

$$k[OH + CH_2(CHONO_2)(R)] \simeq 0.4$$

where, for example, $CH_2(CHONO_2)(R)$ designates a $-CH_2-$ group bonded to a $>CHONO_2$ group and an $-R$ group, where $-R$ is either a $-CH_3$ or a $-CH_2-$ group.

Based on the above group rate constants, and using the $CH_3(CH_2)$ and $CH_2(CH_3)(X)$ [where $X \equiv CH_2$, CH or C] group rate constants derived from the alkanes (Atkinson et al. 1984a), rate constants for the reaction of OH radicals with neopentyl nitrate and cyclohexyl nitrate of 5.7×10^{-13} cm^3 molecule^{-1} sec^{-1} and 4.6×10^{-12} cm^3 molecule^{-1} sec^{-1}, respectively, can be estimated. These estimated values are somewhat lower and higher, respectively (by a factor of ~1.4) than the experimental data given in Table V-1.

In addition, the present OH radical rate constants for 3-nitro-2-methylbutane and 2-nitro-3-methylpentane allow the following group rate constants to be derived:

$$k[OH + CH(CH_3)_2(CHONO_2) = 1.3 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$$

and

$$k[OH + CH(CH_3)(CH_2)(CHONO_2) = 1.1 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$$

Assuming that

$$k[OH + CH_3(CONO_2)] \cong k[OH + CH_3(CHONO_2)] \simeq 0.09 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1},$$

then the rate constant for 2-nitro-2-methylpentane yields

$$k[OH + CH_2(CH_2)(CONO_2)] \simeq 0.2 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$$

These group rate constants are reasonably self-consistent, and allow OH radical reaction rate constants to be estimated for a variety of alkyl nitrates for which no kinetic data are available. For example, although OH radical rate constants are not available for 2-nitro-2-methylbutane, 3-nitro-2-methylpentane and 4-nitro-2-methylpentane, rate constants of ~7 x 10^{-13}, ~2.2 x 10^{-12} and ~3.0 x 10^{-12} cm^3 $molecule^{-1}$ sec^{-1}, respectively, can be estimated from the above data.

The OH radical rate constants for the alkyl nitrates given in Table V-1 and those estimated above can then be used to correct the observed yields of these nitrates from the corresponding alkane for the consumption of these nitrates by reaction with OH radical, as discussed below.

2. Alkyl Nitrate Yields

The initial reactant concentrations and the observed amounts of the alkane consumed and alkyl nitrate formed, as measured at various times during the irradiations, are given in Table V-2.

This and previous (Atkinson et al. 1982c,d) work in these laboratories has shown that reaction with OH radicals is the major loss process for the alkyl nitrates and the alkanes under the conditions of these experiments. Therefore, the alkane and alkyl nitrate concentrations are governed by

$$d[RH]/dt = -k_5[OH][RH] \qquad (VI)$$

$$d[RONO_2]/dt = \alpha k_5[OH][RH] - k_3[OH][RONO_2] \qquad (VII)$$

where k_5 and k_3 are the rate constants for the reactions of OH radicals with the alkanes and the alkyl nitrates, respectively and α are the yields of the alkyl nitrates. Under conditions where the OH radical concentration is constant, these equations can be integrated to obtain

$$[RH]_t = [RH]_o \; e^{-k_5[OH]t} \qquad (VIII)$$

and

$$[RONO]_t = [RH]_o \; \frac{\alpha k_5}{(k_5-k_3)} \left[e^{-k_3[OH]t} - e^{-k_5[OH]t} \right] \qquad (IX)$$

Table V-2. Initial Conditions and Experimental Results for CH_3ONO-NO-Alkane-Air Irradiations

Alkane	Initial Conc (ppb)			-Δ[alkane]	Alkyl Nitrate Yields (ppb)	
	CH_3ONO	NO	Alkane	ppb		
Neopentane					Neopentyl nitrate	
					Obs	Corr[a]
	~1320	~1000	967	27	1.3	1.3
				46	2.4	2.5
				60	3.0	3.1
				74	3.6	3.8
				79	4.0	4.2
	~1080	~1000	1087	43	2.4	2.5
				70	4.0	4.2
				88	4.4	4.6
	~1500	~1000	1018	51	2.8	2.9
				74	3.9	4.1
				97	4.4	4.7
Cyclohexane					Cyclohexyl nitrate	
					Obs	Corr[a]
	~1260	~1000	937	128	18.6	19.2
				211	27.0	28.6
				271	38.2	41.3
				315	43.6	48.0
	~1250	~1000	1000	161	24.5	25.5
				246	35.1	37.5
				293	44.5	48.2
				338	50.3	55.4

continued

Table V-2 (continued) - 2

Alkane	Initial Conc (ppb)			-Δ[alkane]	Alkyl Nitrate Yields (ppb)			
	CH_3ONO	NO	Alkane	ppb				
2-Methylbutane					3-nitro-2-methylbutane		2-nitro-2-methylbutane[b]	
					Obs	Corr[a]	Obs	Corr
	~1360	~1000	899	120	4.3	4.4	3.1	3.1
				185	6.7	7.1	5.1	5.2
				224	7.9	8.4	6.0	6.1
				248	8.6	9.3	6.6	6.8
	~1220	~1000	882	108	3.9	4.0	2.7	2.7
				170	6.2	6.5	4.4	4.5
				204	7.3	7.8	5.3	5.4
				229	8.0	8.6	6.1	6.2
	~1300	~1000	967	112	3.9	4.0	2.8	2.8
				173	6.2	6.5	4.4	4.5
				208	7.5	7.9	5.4	5.5
				234	8.3	8.8	6.2	6.3
2-Methylpentane					2-nitro-2-methylpentane		3-+4-nitro2-methylpentane[c]	
					Obs	Corr[a]	Obs	Corr
	~1220	~1000	905	161	1.1	1.1	16.2	17.0
				239	2.3	2.4	19.0	20.5
				278	3.1	3.3	22.6	24.7
				309	3.4	3.6	25.8	28.6
	~1220	~1000	905	180	2.0	2.1	14.5	15.3
				254	3.3	3.5	21.4	23.2
				298	3.9	4.2	24.0	26.4
				326	-	-	25.3	28.2

continued

Table V-2 (continued) - 3

Alkane	Initial Conc (ppb)			$-\Delta$[alkane]	Alkyl Nitrate Yields (ppb)	
	CH_3ONO	NO	Alkane	ppb		
3-Methylpentane					2-Nitro-3-methylpentane	
					Obs	Corr[a]
	~1240	~1000	879	175	10.4	11.0
				246	15.4	16.9
				281	17.2	19.1
				303	18.4	20.7
	~1320	~1000	938	190	10.1	10.7
				270	15.7	17.2
				348	18.1	20.6
	~950	~10,000	955	37	2.0	2.0
				67	3.5	3.6
				100	4.1	4.2
				130	6.3	6.6

---

[a] Corrected using the OH radical rate constant determined in this work.

[b] Tentative assignment. OH radical rate constant estimated to be ~7 x 10^{-13} cm^3 $molecule^{-1}$ sec^{-1}.

[c] Tentative assignments. OH radical rate constants estimated to be ~2.2 x 10^{-12} and ~3.0 x 10^{-12} cm^3 $molecule^{-1}$ sec^{-1}, respectively.

where $[RH]_o$ is the initial alkane concentration, [OH] is the constant hydroxyl radical concentration, and $[RH]_t$ and $[RONO_2]_t$ are the alkane and alkyl nitrate concentrations, respectively, at time t. Equations (VIII) and (IX) can be combined to obtain

$$\alpha = F \left\{ \frac{[RONO_2]_t}{\Delta[RH]_t} \right\} \qquad \text{(X)}$$

where

$$F = \left(\frac{k_5 - k_3}{k_5} \right) \left[\frac{1 - \dfrac{[RH]_t}{[RH]_o}}{\left(\dfrac{[RH]_t}{[RH]_o} \right)^{\frac{k_3}{k_5}} - \left(\dfrac{[RH]_t}{[RH]_o} \right)} \right] \qquad \text{(XI)}$$

and $\Delta[RH]_t = ([RH]_o - [RH]_t)$. Note that the correction factor F does not have any dependence on the OH radical concentration, and thus equation (XI) might be expected to be valid even under conditions where [OH] is not constant throughout the experiment, as was the case for the irradiations carried out in this work. Computer simulations indeed showed that the use of these equations introduced a totally negligible error in accounting for the OH radical reactions with the alkyl nitrates.

Equations (X) and (XI) were used to correct each of the data points for each alkyl nitrate isomer given in Table V-2. F was calculated using the experimentally observed amounts of n-alkanes consumed and the values of k_5 and k_3 obtained from recent kinetic studies from these laboratories (Atkinson et al. 1984a) or from this work. The largest correction corresponded to a value of F of 1.14, and in most cases these corrections were relatively minor.

Typical plots of the total corrected alkyl nitrate yields against the amount of n-alkane reacted are shown in Figures V-3 to V-5. It can be seen from these figures that straight line plots with zero intercepts were obtained. Table V-3, lists the least squares slopes obtained from such plots, which can be identified with the fraction of the n-alkane reacted yielding the observed alkyl nitrates.

As noted in Table V-3, in two of these cases the postulated alkyl nitrates are based upon tentative identifications. Thus in the CH_3ONO-NO-

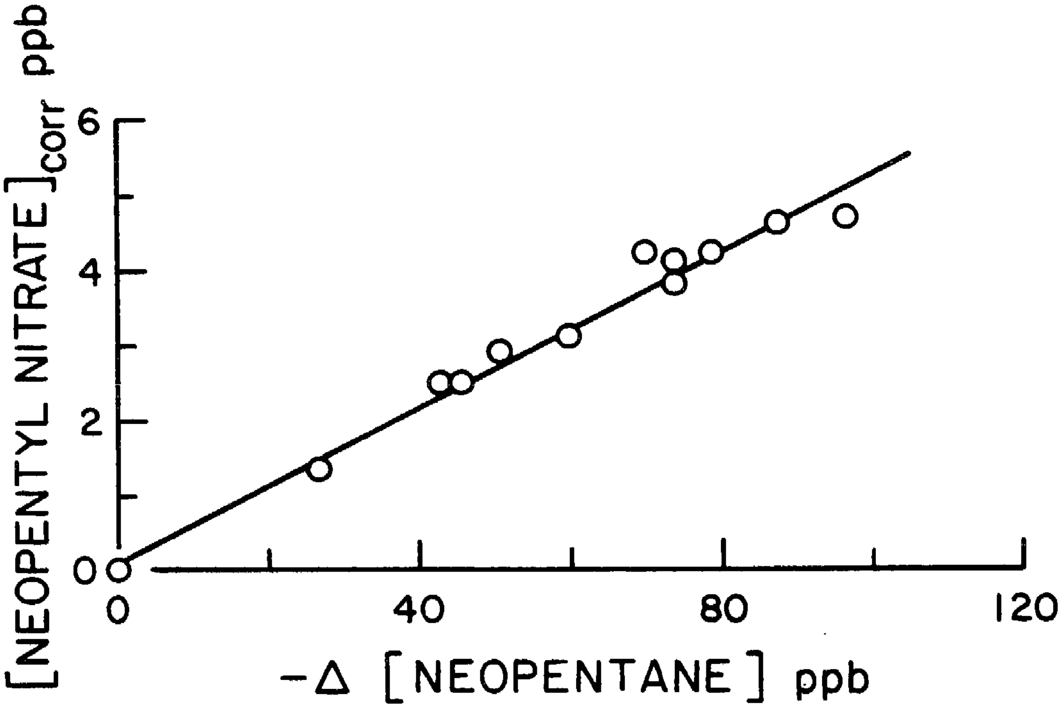


Figure V-3. Plot of the neopentyl nitrate yields, corrected for reaction with OH radicals, against the amount of neopentane consumed.

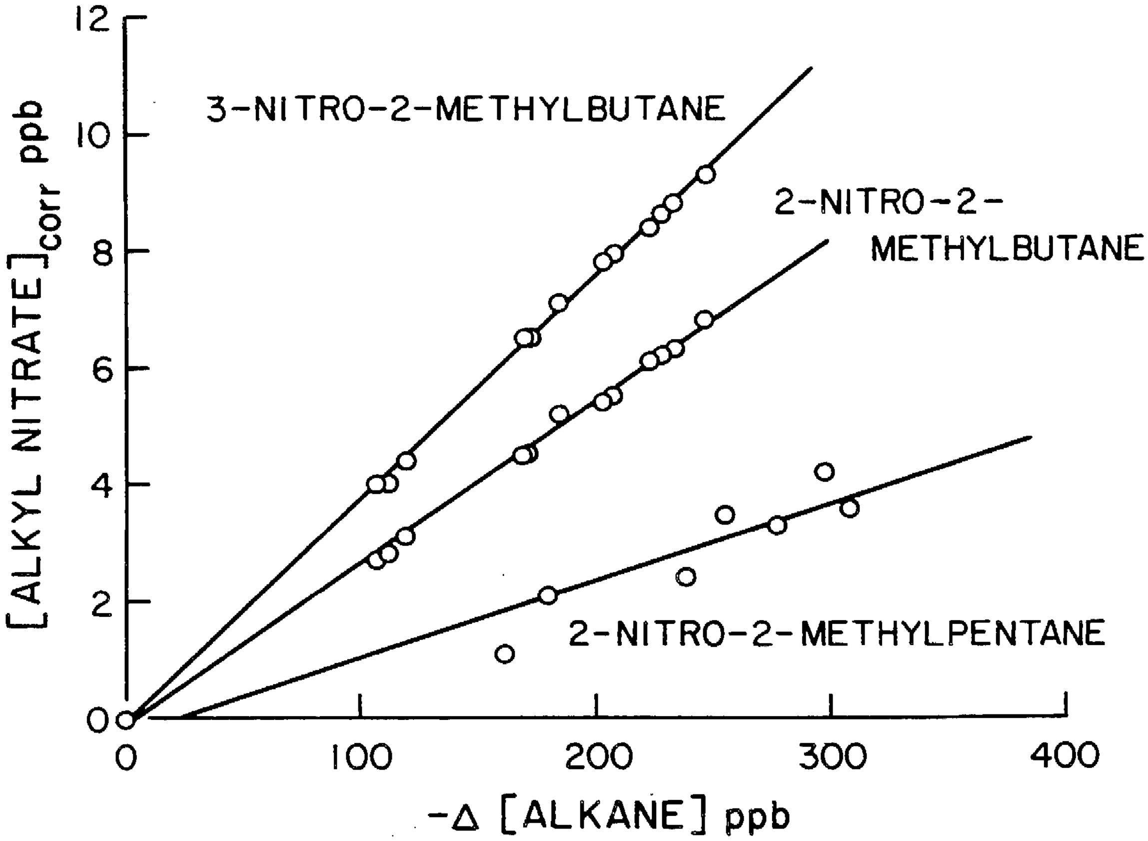


Figure V-4. Plot of the alkyl nitrate yield, corrected for reaction with OH radicals, against the amount of alkane consumed for 2- and 3-nitro-2-methylbutane and 2-nitro-2-methylpentane.

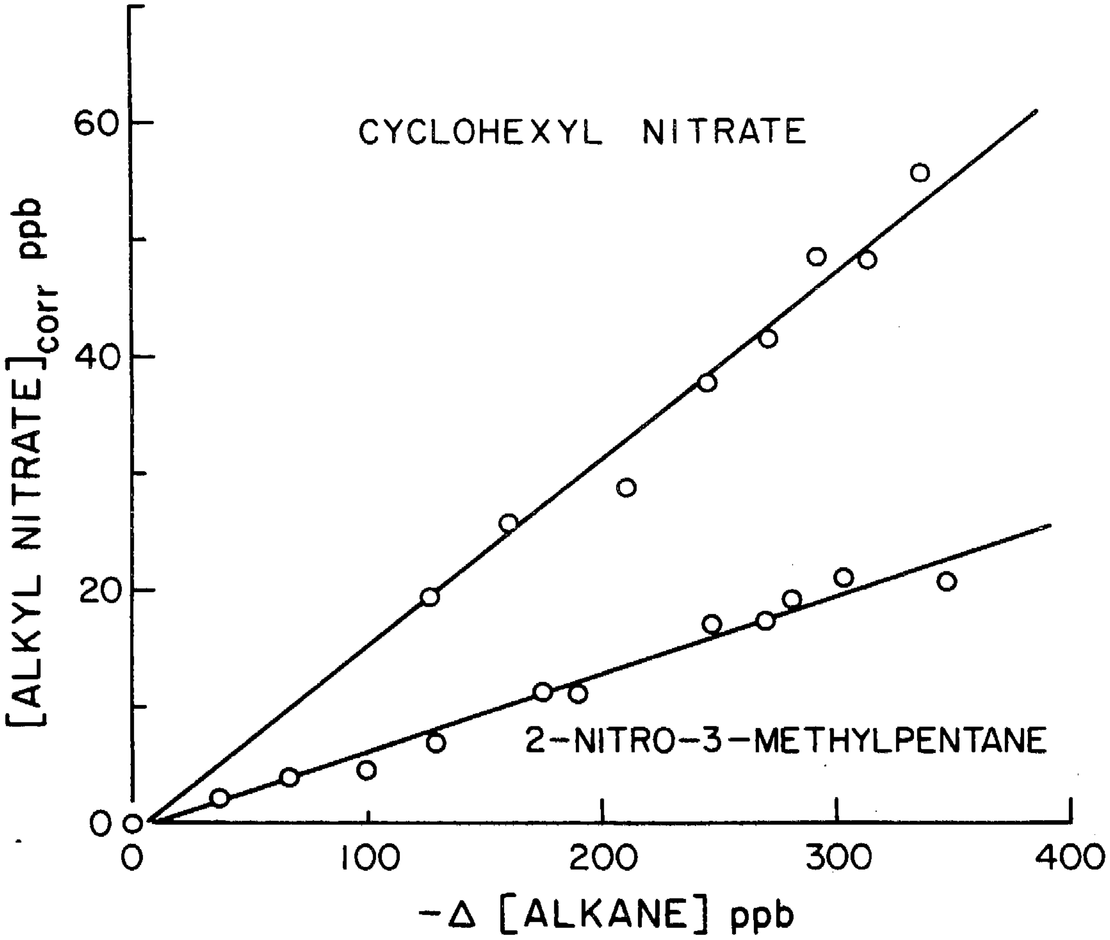


Figure V-5. Plot of the alkyl nitrate yield, corrected for reaction with OH radicals, against the amount of alkane consumed, for cyclohexyl nitrate and 2-nitro-3-methylpentane.

Table V-3. Yields of Alkyl Nitrates at 298 ± 2 K and 735 Torr Total Pressure

Alkane	Alkyl Nitrate	Yield [a]	% RO_2 Formed	$k_2/(k_1 + k_2)$
Neopentane	Neopentyl nitrate	0.0513 ± 0.0053	100	0.0513 ± 0.0053
Cyclohexane	Cyclohexyl nitrate	0.160 ± 0.015	100	0.160 ± 0.015
2-Methylbutane	3-Nitro-2-methylbutane	0.0381 ± 0.0009	35	0.109 ± 0.003
	2-Nitro-2-methylbutane[c]	0.0277 ± 0.0011	52	0.0533 ± 0.0022
2-Methylpentane	2-Nitro-2-methylpentane	0.0133 ± 0.0036	38	0.0350 ± 0.0096
	3-Nitro-2-methylpentane +4-Nitro-2-methylpentane [c]	0.0874 ± 0.0083	53	0.165 ± 0.016
3-Methylpentane	2-Nitro-3-methylpentane	0.0671 ± 0.0064	48	0.140 ± 0.014

[a] Observed yields, i.e., (d[alkyl nitrate]/-d[alkane]). Indicated errors are two least squares standard deviations of the plots shown in Figures V-3 to V-5.

[b] % of the individual RO_2 radicals formed during the reaction of OH radicals with the alkane (see text).

[c] Tentative identification.

air irradiations of 2-methylbutane and 2-methylpentane, gas chromatographic peaks were observed which increased linearly with the amount of alkane consumed, and which were not due to the expected carbonyl products (e.g., acetone and acetaldehyde from 2-methylbutane and acetone, propionaldehyde, acetaldehyde and isobutyraldehyde from 2-methylpentane). These gas chromatographic peaks were thus attributed to the other expected alkyl nitrates formed from these alkanes, and the GC-FID calibration factors were taken to be equal to those for their isomers. The yields of these tentatively assigned alkyl nitrates are also given in Tables V-2 and V-3.

The only literature data concerning the formation of these alkyl nitrates from their corresponding alkyl peroxy radicals are those of Takagi et al. (1981) for cyclohexyl nitrate formation from cyclohexane. The cyclohexyl nitrate yield from cyclohexane determined by Takagi et al. (1981) using Fourier transform infrared absorption spectroscopic analyses was 9.0 ± 8.8%, which can be compared with our present value of 16.0 ±

1.6% (where in both cases the indicated errors are two least squares standard deviations). While the agreement is not good, the values do overlap within their stated error limits.

As discussed previously (Atkinson et al. 1982a, 1983a) the major reactions occurring in the CH_3ONO-NO-alkane-air photolysis system are as follows:

$$CH_3ONO + h\nu \rightarrow CH_3O + NO$$

$$CH_3O + O_2 \rightarrow HCHO + HO_2$$

$$HO_2 + NO \rightarrow OH + NO_2$$

$$OH + RH \rightarrow R + H_2O \tag{5}$$

$$R + O_2 \xrightarrow{M} RO_2 \tag{6}$$

$$RO_2 + NO \rightarrow RO + NO_2 \tag{1}$$

$$\xrightarrow{M} RONO_2 \tag{2}$$

$$RO + NO_2 \xrightarrow{M} RONO_2 \tag{7}$$

$$RO \xrightarrow[\downarrow NO_2]{O_2\ \ NO} OH + \text{oxygenated products} \tag{8}$$

$$OH + RONO_2 \rightarrow \text{products} \tag{3}$$

In this system the alkanes and the alkyl nitrates are consumed essentially solely by reaction with OH radicals [reactions (5) and (3)]. The only significant sink for the alkyl peroxy radicals formed from the reaction of OH radicals with the alkanes is reaction with NO, forming either the corresponding alkyl nitrate [reaction (2)] or the alkoxy radical [reaction (1)], since the reactions of alkyl peroxy radicals with NO_2 forming alkyl peroxynitrates (RO_2NO_2) are insignificant due to the rapid back-decomposition of the alkyl peroxynitrates (Atkinson and Lloyd 1984).

The formation of alkyl nitrates can occur either from the reaction of alkyl peroxy radicals with NO [reaction (2)] or from the reaction of alkoxy radicals with NO_2 [reaction (7)]. However, under the conditions of our experiments, secondary alkoxy radicals will primarily react with O_2, decompose or isomerize (Atkinson and Lloyd 1984), while the tertiary alkoxy radicals will primarily decompose or isomerize (Atkinson and Lloyd 1984).

Upper limits for the contribution of reaction (1) to the observed alkyl nitrate yields for these experiments can be estimated from the rate constants for the reactions of alkoxy radicals with NO_2 and O_2, and the NO_2 and O_2 concentrations. Alkoxy radicals react with NO_2 with a rate constant of $k_1 \approx 1.5 \times 10^{-11}$ cm^3 molecule^{-1} sec^{-1} at room temperature and atmospheric pressure (Atkinson and Lloyd 1984). The reactions of alkoxy radicals with O_2 have received little direct attention, but recently Gutman et al. (1982) have determined a rate constant of 8×10^{-15} cm^3 molecule^{-1} sec^{-1} at 296 K for the reaction

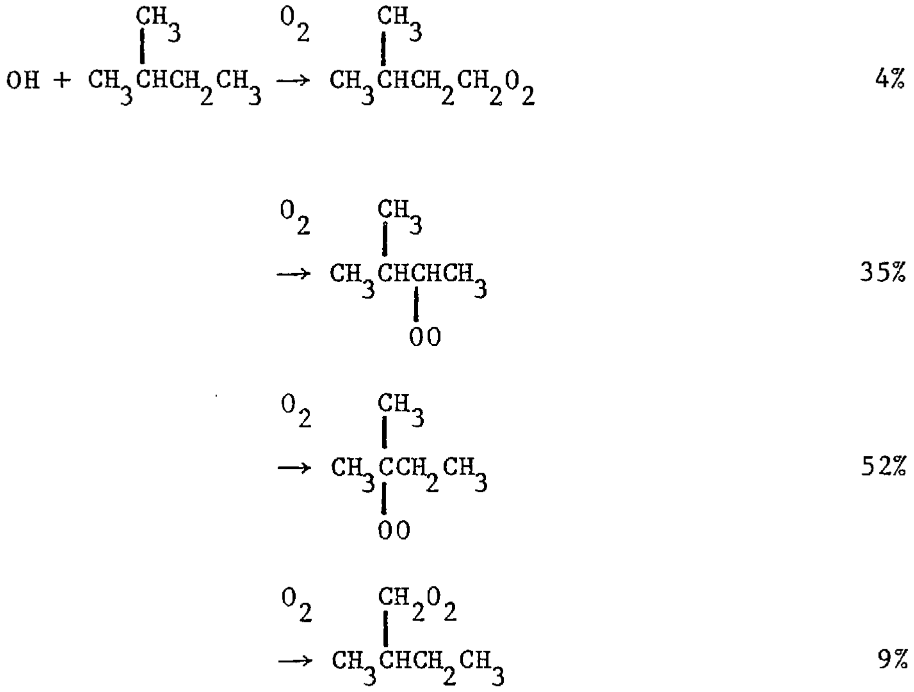
$$C_2H_5O + O_2 \rightarrow CH_3CHO + HO_2$$

Furthermore, from thermochemical considerations, Gutman et al. (1982) have derived rate constants at room temperature for the reaction of 1-alkoxy radicals with O_2 of $\sim 7 \times 10^{-15}$ cm^3 molecule^{-1} sec^{-1}, with the 2-propoxy and 2-butoxy radicals reacting ~1.5 to 5 times faster. Hence, assuming a maximum of 2 ppm of NO_2 in these experiments (based on the total initial concentrations of nitrogen-containing species, e.g. NO and CH_3ONO, which can yield NO_2), and considering only the reactions of RO radicals with O_2 and NO_2, then a maximum yield of alkyl nitrate formation from the reaction of RO radicals with NO_2 of 1.8% can be calculated for 1-alkyl nitrates, with yet lower maximum yields for the secondary alkyl nitrates. Since (a) all the initial nitrogenous species are not converted to NO_2 during NO_x-organic-air irradiations, (b) larger ($\geq C_4$) alkoxy radicals undergo significant decomposition and isomerization reactions (Atkinson and Lloyd 1984) and (c) the secondary alkoxy radicals undergo faster reaction with O_2, it may be concluded that less than one percent of the observed secondary alkyl nitrate yields are due to the reaction of the corresponding secondary alkoxy radicals with NO_2 in the CH_3ONO-NO-alkane-air irradiations carried out in this study.

For the two tertiary alkoxy radicals, the decomposition rates for $(CH_3)_2C(O)C_2H_5$ and $(CH_3)_2C(O)C_3H_7$ are ~5 x 10^4 sec^{-1} and >5 x 10^4 sec^{-1}, respectively, at 298 K and atmospheric pressure (Batt 1979). Thus for these tertiary alkoxy radicals, the fractional yield of alkyl nitrate formed from reaction (7) can be estimated to be $\lesssim$0.015 under the present experimental conditions. Hence the formation of alkyl nitrates from combination of the alkoxy radical with NO_2 is minor, and thus the observed alkyl nitrate yields are essentially entirely due to formation via reaction (2). This was substantiated by the results from a CH_3ONO-NO-3-methylpentane-air irradiation in which the final (NO_x-NO) of 2.2 ppm, assumed to be mainly NO_2 since the initial CH_3ONO would have been photolyzed after this irradiation period (~89 min), was a factor of 1.5-2 higher than in other irradiations, but the 2-nitro-3-methylpentane yield was indistinguishable from the data obtained at lower final (NO_x-NO) levels (Table V-2).

Thus the alkyl nitrate yields tabulated in Tables V-2 and V-3 correspond to their formation from the reaction of the corresponding alkyl peroxy radicals with NO [reaction (2)]. In order to derive the rate constant ratios $k_2/(k_1 + k_2)$ for the individual alkyl peroxy radicals from the observed overall yields, it is necessary to determine the fraction of the overall OH radical reaction with the parent alkane which gave rise to the individual alkyl peroxy radicals.

From our previous studies of the kinetics of OH radical reaction with alkanes (Atkinson et al. 1982d, 1984a), the fraction of the overall OH radical reactions with the alkanes yielding the individual alkyl peroxy radicals can be estimated. Thus, for example, based upon the data of Atkinson et al. (1984a) the OH radical reaction for 2-methylbutane proceeds (after O_2 addition to the initially formed alkyl radicals) to yield the following distribution of alkyl peroxy radicals:



$$\mathrm{OH + CH_3\overset{CH_3}{\overset{|}{C}}HCH_2CH_3 \xrightarrow{O_2} CH_3\overset{CH_3}{\overset{|}{C}}HCH_2CH_2O_2}\qquad 4\%$$

$$\mathrm{\xrightarrow{O_2} CH_3\overset{CH_3}{\overset{|}{C}}H\underset{\underset{OO}{|}}{C}HCH_3}\qquad 35\%$$

$$\mathrm{\xrightarrow{O_2} CH_3\overset{CH_3}{\overset{|}{\underset{\underset{OO}{|}}{C}}}CH_2CH_3}\qquad 52\%$$

$$\mathrm{\xrightarrow{O_2} CH_3\overset{CH_2O_2}{\overset{|}{C}}HCH_2CH_3}\qquad 9\%$$

Thus the yields of the individual alkyl nitrates [i.e., the rate constant ratios $k_2/(k_1 + k_2)$] from their parent alkyl peroxy radicals can be readily estimated, and these data are also given in Table V-3.

The rate constant ratios $k_2/(k_1 + k_2)$ for these individual primary, secondary and tertiary alkyl peroxy radicals are compared in Table V-4 with our previous data for the alkyl peroxy radicals formed from the C_2-C_8 n-alkanes (Atkinson et al. 1982a, 1983a). It can be seen from this table that for the secondary alkyl peroxy radicals these rate constant ratios increase monotonically with the carbon number of the RO_2 radical (from ~0.04 for C_3 to ~0.33 for C_8), and to a first approximation are reasonably consistent for a given set of alkyl peroxy radicals of the same carbon number. This is most apparent for the secondary C_6 alkyl peroxy radicals generated from n-hexane, cyclohexane, 2-methylpentane and 3-methylpentane, with the rate constant ratios $k_2/(k_1 + k_2)$ ranging from 0.14 to 0.22. However, there do appear to be differences in the $k_2/(k_1 + k_2)$ ratios within these various secondary C_6 alkyl peroxy radicals, with the most branched radicals having the lower rate constant ratios.

It is also apparent from Table V-4, as proposed previously (Atkinson et al. 1982a), that the rate constant ratios for primary alkyl peroxy radicals are at least a factor of 2 lower than those for secondary

Table V-4. Rate Constant Ratios $k_2/(k_1 + k_2)$ for Individual Alkyl Peroxy (RO_2) Radicals at 299 ± 2 K and 735-740 Torr Total Pressure

	Primary		Secondary		Tertiary	
Alkane	RO_2	$k_2/(k_1 + k_2)$	RO_2	$k_2/(k_1 + k_2)$	RO_2	$k_2/(k_1 + k_2)$
Ethane[a]	ethyl	$\lesssim 0.014$				
Propane[a]	1-propyl	0.020 ± 0.009	2-propyl	0.043 ± 0.003	-	-
n-Butane[a]	1-butyl	$\lesssim 0.040$	2-butyl	0.090 ± 0.009	-	-
n-Pentane[a,b]	-		2-pentyl	0.129 ± 0.014	-	-
	-		3-pentyl	0.118 ± 0.014	-	-
Neopentane	neopentyl	0.0513 ± 0.0053				
2-Methylbutane			2-methyl-3-butyl	0.109 ± 0.003	2-methyl-2-butyl	0.0533 ± 0.0022
n-Hexane[a]			2-hexyl	0.220 ± 0.034		
			3-hexyl	0.219 ± 0.029		
Cyclohexane			cyclohexyl	0.160 ± 0.015		
2-Methylpentane			2-methyl-3-pentyl +2-methyl-4-pentyl	0.165 ± 0.016	2-methyl-2-pentyl	0.0350 ± 0.0096
3-Methylpentane			3-methyl-2-pentyl	0.140 ± 0.014		
n-Heptane[a,b]			2-heptyl	0.324 ± 0.044		
			3-heptyl	0.312 ± 0.041		
			4-heptyl	0.290 ± 0.037		
n-Octane[a]			2-octyl	0.353 ± 0.027		
			3-octyl	0.343 ± 0.031		
			4-octyl	0.324 ± 0.032		

[a] Calculated from the data of Atkinson et al. (1982a).

[b] Calculated from the data of Atkinson et al. (1982a, 1983a).

alkyl peroxy radicals of the same carbon number (compare the rate constant ratio $k_2/(k_1 + k_2)$ for 1-propyl peroxy versus that for 2-propyl peroxy, and that for neopentyl peroxy versus those for the secondary C_5 alkyl peroxy radicals). This work further shows for the first time that the rate constant ratios $k_2/(k_1 + k_2)$ for tertiary alkyl peroxy radicals are also markedly lower, by factors of ~3-5, than are those for the corresponding secondary alkyl peroxy radicals.

The reasons for these differences in the rate constant ratios $k_2/(k_1 + k_2)$ for primary, secondary and tertiary alkyl peroxy radicals are not known at present. However, the data given in Table V-4 and discussed above allow approximate a-priori estimates to be made for alkyl nitrate formation yields from the various alkyl peroxy radicals involved in alkane degradation pathways under atmospheric conditions. This predictive scheme will thus allow cost-effective estimates of the alkyl nitrate yields from the reaction of RO_2 radicals with NO, an important input into the chemical computer sub-models of trajectory or grid airshed models.

VI. REFERENCES

Atkinson, R., Darnall, K. R., Lloyd, A. C., Winer, A. M. and Pitts, J. N., Jr. (1979): Kinetics and mechanisms of the reaction of the hydroxyl radical with organic compounds in the gas phase. In: Advances in Photochemistry, J. N. Pitts Jr., G. S. Hammond and K. Gollnick, Eds., John Wiley & Sons, NY, Vol. 11, p. 375.

Atkinson, R., Carter, W. P. L., Darnall, K. R., Winer, A. M. and Pitts, J. N., Jr. (1980): A smog chamber and modeling study of the gas phase NO_x-air photooxidation of toluene and the cresols. Int. J. Chem. Kinet., 12, 779.

Atkinson, R., Aschmann, S. M., Winer, A. M. and Pitts, J. N., Jr. (1981a): Rate constants for the gas phase reactions of O_3 with a series of carbonyls at 296 K. Int. J. Chem. Kinet., 13, 1133.

Atkinson, R., Carter, W. P. L., Winer, A. M. and Pitts, J. N., Jr. (1981b): An experimental protocol for the determination of OH radical rate constants with organics using methyl nitrite photolysis as an OH radical source. J. Air Pollut. Control Assoc., 31, 1090.

Atkinson, R., Aschmann, S. M., Carter, W. P. L., Winer, A. M. and Pitts, J. N., Jr. (1982a): Alkyl nitrate formation from the NO_x-air photooxidations of C_2-C_8 n-alkanes. J. Phys. Chem., 86, 4563.

Atkinson, R., Aschmann, S. M., Winer, A. M. and Pitts, J. N., Jr. (1982b): Rate constants for the reaction of OH radicals with a series of alkanes and alkenes at 299 ± 2 K. Int. J. Chem. Kinet., 14, 507.

Atkinson, R., Aschmann, S. M., Carter, W. P. L. and Winer, A. M. (1982c): Kinetics of the gas-phase reactions of OH radicals with alkyl nitrates at 299 ± 2 K. Int. J. Chem. Kinet., 14, 919.

Atkinson, R., Aschmann, S. M., Carter, W. P. L., Winer, A. M. and Pitts, J. N., Jr. (1982d): Kinetics of the reactions of OH radicals with n-alkanes at 299 ± 2 K. Int. J. Chem. Kinet., 14, 781.

Atkinson, R., Lloyd, A. C. and Winges, L. (1982e): An updated chemical mechanism for hydrocarbon/NO_x/SO_2 photooxidations suitable for inclusion in atmospheric simulation models. Atmos. Environ., 16, 1341.

Atkinson, R., Carter, W. P. L. and Winer, A. M. (1983a): Effects of temperature and pressure on alkyl nitrate yields in the NO_x photooxidations of n-pentane and n-heptane. J. Phys. Chem., 87, 2012.

Atkinson, R., Aschmann, S. M. and Carter, W. P. L. (1983b): Kinetics of the reactions of O_3 and OH radicals with furan and thiophene at 298 ± 2 K. Int. J. Chem. Kinet., 15, 51.

Atkinson, R., Carter, W. P. L. and Winer, A. M. (1983c): Effects of pressure on product yields in the NO_x photooxidations of selected aromatic hydrocarbons. J. Phys. Chem., 87, 1605.

Atkinson, R. and Carter, W. P. L. (1984): Kinetics and mechanisms of the gas phase reactions of ozone with organic compounds under atmospheric conditions. Chem. Rev., 84, 437.

Atkinson, R. and Lloyd, A.C. (1984): Evaluation of kinetic and mechanistic data for modeling of photochemical smog. J. Phys. Chem. Ref. Data, 13, 315.

Atkinson, R., Carter, W. P. L., Aschmann, S. M., Winer, A. M. and Pitts, J. N., Jr. (1984a): Kinetics of the reactions of OH radicals with a series of branched alkanes at 297 ± 2 K. Int. J. Chem. Kinet., 16, 469.

Atkinson, R., Plum, C. N., Carter, W. P. L, Winer, A. M. and Pitts, J. N., Jr. (1984b): Rate constants for the gas phase reactions of NO_3 radicals with a series of organics in air at 298 ± 1 K. J. Phys. Chem., 88, 1210.

Bandow, H., Washida, N. and Akimoto, H. (1983): Paper presented at the 11th International Conference on Photochemistry, University of Maryland, College Park, MA, August 21-26.

Batt, L. (1979): The gas-phase decomposition of alkoxy radicals. Int. J. Chem. Kinet., 11, 977.

Biermann, H. W., Harris, G. W. and Pitts, J. N., Jr. (1982): Photoionization mass spectrometer studies of the collisionally stabilized product distribution in the reaction of OH radicals with selected alkenes at 298 K. J. Phys. Chem., 86, 2958.

Black, F. M., High, L. E. and Lang, J. M. (1980): Composition of automobile evaporative and tailpipe hydrocarbon emissions. J. Air Pollut. Control Assoc., 30, 1216.

Carter, W. P. L., Ripley, P. S., Smith, C. G. and Pitts, J. N., Jr. (1981): Atmospheric chemistry of hydrocarbon fuels. Vol. 1, Experiments, Results and Discussion, USAF Final Report ESL-TR-81-53, November.

Caswell, R. L., Debold, K. J. and Gilbert, L. S., Eds. (1981): Pesticide Handbook (Entoma). 29th edn. Entomological Society of America, College Park, MD, 286 pp.

Criegee, R. (1975): Mechanism of ozonolysis. Angew. Chem., Int. Ed. Engl., 14, 745.

Crutzen, P. J. (1982): The global distribution of hydroxyl. In: Atmospheric Chemistry, E. D. Goldberg, Ed., Springer-Verlag, Berlin, p. 313.

Darnall, K. R., Carter, W. P. L., Winer, A. M., Lloyd, A. C. and Pitts, J. N., Jr. (1976): Importance of RO_2 + NO in alkyl nitrate formation from C_4-C_6 alkane photooxidation under simulated atmospheric conditions. J. Phys. Chem., 80, 1948.

Darnall, K. R., Atkinson, R. and Pitts, J. N., Jr. (1979): Observation of biacetyl from the reaction of OH radicals with o-xylene. Evidence for ring cleavage. J. Phys. Chem., 83, 1943.

Finlayson-Pitts, B. J. and Pitts, J. N., Jr. (1977): The chemical basis of air quality: kinetics and mechanisms of photochemical air pollution and application to control strategies. In: Advances in Environmental Science and Technology., 7, J. N. Pitts, Jr. and R. L. Metcalf, Eds., Wiley-Interscience, NY, p. 75.

Fleck, R. (1983): Food Protection and Toxicology Center, University of California, Davis, California. Private communication.

Gay, B. W., Jr., Hanst, P. L., Bufalini, J. J. and Noonan, R. C. (1976): Atmospheric oxidation of chlorinated ethylenes. Environ. Sci. Technol, 10, 58.

Greiner, N. R. (1970): Hydroxyl radical kinetics by kinetic spectroscopy. VI. Reactions with alkanes in the range 300-500 degrees K. J. Chem. Phys., 53, 1070.

Gutman, D., Sanders, N. and Butler, J. E. (1982): Kinetics of the reactions of methoxy and ethoxy radicals with oxygen. J. Phys. Chem., 86, 66.

Harding, L. B. and Goddard, W. A., III (1978): Mechanisms of gas-phase and liquid-phase ozonolysis. J. Am. Chem. Soc., 100, 7180.

Hendry, D. G. and Kenley, R. A. (1979): Atmospheric reaction products of organic compounds. U. S. Environmental Protection Agency Publication No. EPA-560/12-79-001, Research Triangle Park, NC, June.

Herron, J. T., Huie, R. E. and Hodgeson, J. A., Eds. (1979): Chemical kinetic data needs for modeling the lower troposphere. National Bureau of Standards Special Publication 557, August.

Herron, J. T., Martinez, R. I., Huie, R. E. (1982): Kinetics and energetics of the Criegee intermediate in the gas phase. I. The Criegee intermediate in ozone-alkene reactions. Int. J. Chem. Kinet., 14, 201-224.

Hisatsune, I. C. and Heicklen, J. (1973): Infrared spectrum of formyl chloride. Can. J. Spectrosc., 18, 77.

Jensen, R. J. and Pimentel, G. C. (1967): Kinetics of decomposition of chloroformic acid by rapid-scan infrared spectroscopy. J. Phys. Chem., 71, 1803.

Kenley, R. A., Davenport, J. E. and Hendry, D. G. (1981): Gas-phase hydroxyl radical reactions. Products and pathways for the reaction of OH with aromatic hydrocarbons. J. Phys. Chem., 85, 2740.

Killus, J. P. and Whitten, G. Z. (1982): A mechanism describing the photochemical oxidation of toluene in smog. Atmos. Environ., 16, 1973.

Leone, J. A. and Seinfeld, J. H. (1984): Updated chemical mechanism for atmospheric photooxidation of toluene. Int. J. Chem. Kinet., 16, 159.

Martinez, R. I., Herron J. T., and Huie, R. E. (1981): The mechanism of ozone-alkene reactions in the gas phase. A mass spectrometric study of the reactions of eight linear and branched-chain alkenes. J. Am. Chem. Soc., 103, 3807.

Moilanen, K. W., Crosby, D. G., Soderquist, C. J. and Wong, A. S. (1975): Dynamic aspects of pesticide photodecomposition. In: Environmental Dynamics of Pesticides, R. Haque and V. H. Freed, Eds., Plenum Press, p. 45.

Nicovich, J. M., Thompson, R. L. and Ravishankara, A. R. (1981): Kinetics of the reactions of the hydroxyl radical with xylenes. J. Phys. Chem., 85, 2913.

Niki, H., Maker, P. D., Savage, C. M., Breitenbach, L. P., Martinez, R. I., and Herron, J. T. (1982): A Fourier transform infrared study of the gas-phase reactions of O_3 with chloroethylenes. Detection of peroxyformic acid. J. Phys. Chem., 86, 1858.

Paraskevopoulos, G. and Nip, W. S. (1980): Rates of OH radical reactions. VII. Reactions of OH and OD radicals with n-C_4H_{10}, n-C_4D_{10}, H_2 and D_2, and of OH with neo-C_5H_{12} at 297 K. Can. J. Chem., 58, 2146.

Perry, R. A., Atkinson, R. and Pitts, J. N., Jr. (1976): Rate constants for the reaction of OH radicals with n-butane over the temperature range 297-420 K. J. Chem. Phys., 64, 5314.

Perry, R. A., Atkinson, R. and Pitts, J. N., Jr. (1977a): Rate constants for the reaction of OH radicals with dimethyl ether and vinyl methyl ether over the temperature range 299-427 K. J. Chem. Phys., 67, 611.

Perry, R. A., Atkinson, R. and Pitts, J. N., Jr. (1977b): Kinetics and mechanism of the gas phase reaction of OH radicals with aromatic hydrocarbons over the temperature range 296-478 K. J. Phys. Chem., 81, 296.

Pitts, J. N., Jr. (1983): Reactive species in the gas phase atmospheric photooxidations of volatile pesticide. Presented at the 185th National American Chemical Society Meeting, Pesticide Chemistry Symposium, Seattle, WA, March 20-25.

Plum, C. N., Sanhueza, E., Carter, W. P. L., Atkinson, R., Winer, A. M. and Pitts, J. N., Jr. (1983): OH radical rate constants and photolysis rates of α-dicarbonyls. Environ. Sci. Technol., 17, 479.

Singh, H. B., Ludwig, F. L., and Johnson, W. B. (1978): Tropospheric ozone: Concentrations and variabilities in clean remote atmospheres. Atmos. Environ., 12, 2185.

Stuhl, F. (1973): Rate constant for the reaction of OH with n-C_4H_{10}. Z. Naturforsch, 28A, 1383.

Takagi, H., Washida, N., Akimoto, H., Nagasawa, K., Usui, Y. and Okuda, M. (1980): Photooxidation of o-xylene in the NO-H_2O-air system. J. Phys. Chem., 84, 478.

Takagi, H., Washida, N., Bandow, H., Akimoto, H. and Okuda, M. (1981): Photooxidation of C_5-C_7 cycloalkanes in the NO-H_2O-air system. J. Phys. Chem., 85, 2701.

Taylor, W. D., Allston, T. D., Moscato, M. J., Fazekas, G. B., Kozlowski, R. and Takacs, G. A. (1980): Atmospheric photodissociation lifetimes for nitromethane, methyl nitrite and methyl nitrate. Int. J. Chem. Kinet., 12, 231.

Tully, F. P., Ravishankara, A. R., Thompson, R. L., Nicovich, J. M., Shah, R. C., Kreutter, N. M. and Wine, P. H. (1981): Kinetics of the reactions of hydroxyl radical with benzene and toluene. J. Phys. Chem., 85, 2262.

Winer, A. M., Graham, R. A., Doyle, G. J., Bekowies, P. J., McAfee, J. M., Pitts, J. N., Jr. (1980): An evacuable thermostatted environmental chamber and solar simulator facility for the study of atmospheric chemistry. In: Advances in Environmental Science and Technology, J. N. Pitts, Jr. and R. L. Metcalf, Eds., John Wiley & Sons, NY, Vol. 10, p. 461.

Worthing, C. R., Ed. (1979): The Pesticide Manual. British Crop Protection Council, Lavenham Press Ltd., Suffolk, England, 655 pp.