FORMATION AND FATE OF TOXIC CHEMICALS
IN CALIFORNIA'S ATMOSPHERE

Final Report
Contract No. A2-115-32
California Air Resources Board
July 1984

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ABSTRACT

Although the atmospheric chemistry of NOx/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 O3 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 (ClCH2CHO).

With respect to the chloroethylenes reaction of vinyl chloride with OH radicals gave an ~100% yield of formyl chloride (\(\text{H}^\rightarrow\text{Cl}^\rightarrow\text{C}=\text{O}\)), a toxic
photolabile species while trichloroethylene formed both phosgene (COCl₂) 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 α- 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 (RONO₂) yields were determined for a series of NOₓ-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

\[ M \]
\[ RO₂ + NO \rightarrow RONO₂ \]

is a removal process for both NOₓ 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.
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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.
The statements and conclusions in this report are those of the contractor and not necessarily those of the California Air Resources Board. The mention of commercial products, their source or their use in connection with material reported herein is not to be construed as either an actual or implied endorsement of such products.
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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 O₃, 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 (≥C$_6$) are major constituents of diesel fuels.

During our previous ARB program (Contract No. Al-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-dichloro-propene isomers. These are widely used as agricultural insecticides in California under a variety of trade names.

- To investigate the atmospheric chemistry of three toxic chloro-ethylenes, 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-k evacuatable 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 $1.31 \times 10^{-11}$ cm$^3$ molecule$^{-1}$ sec$^{-1}$, respectively. The analogous rate constants for reaction of these isomers with ozone were determined to be $(1.5 \pm 0.5)$ and $(6.7 \pm 0.8) \times 10^{-19}$ 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 $\geq$13 days is estimated for a 24-hr average OH radical concentration of $1 \times 10^6$ 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$_2$CHO). Whereas
formyl chloride is known to eventually decompose and hydrolyze to CO, HCl, and HCOOH, the other toxic product chloroacetylene 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:

$$\text{OH} + \text{CH}_2=\text{CHCl} \rightarrow \text{HCHO} + \text{HC(O)Cl} + \text{HO}_2$$

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 COCl₂ 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 $\text{NO}_x$-air photooxidations of neopentane, cyclohexane, 2-methylbutane, 2-methyl-
pentane 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

\[
M + RO_2 + NO \rightarrow RONO_2
\]

is a removal process for both NO\textsubscript{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 organic compounds. 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\textsubscript{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-ClCH₂CH=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 >50% of the two isomers of 1,3-dichloropropene plus 1,2-dichloropropene (CH₃CHClCH₂Cl) and related C₃ compounds (Worthing 1979). Other formulations include those by Dow Chemical Co. under the trademarks "Telone" (78.5% 1,3-dichloropropene, 20.5% 1,2-dichloropropene and related compounds), "Telone II" (92% 1,3-dichloropropene), and "Telone Cl7" (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 (O₃), the hydroxyl (OH) radical, and the nitrate (NO₃) 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 >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 O₃ 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:

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

(1)

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

(2)

and hence

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

(1)

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 ($[\text{reactant}]/[O_3]_{\text{initial}} \geq 10$), the reactant concentration remains essentially constant throughout the reaction, and equation (1) may be rearranged to yield:
\[
\frac{-d\ln[O_3]}{dt} = k_1 + k_2[\text{reactant}]
\] (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 \(\sim 160-\ell\) 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 \(\sim 1\) minute. Initial \(O_3\) concentrations after mixing were typically \(\sim 1\) ppm (1 ppm = \(2.41 \times 10^{13}\) 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 cis- and trans-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:

\[
\begin{align*}
\text{CH}_3\text{ONO} + \text{hv} & \rightarrow \text{CH}_3\text{O} + \text{NO} \\
\text{CH}_3\text{O} + \text{O}_2 & \rightarrow \text{HCHO} + \text{HO}_2 \\
\text{HO}_2 + \text{NO} & \rightarrow \text{OH} + \text{NO}_2
\end{align*}
\]
In order to minimize the formation of \( \text{O}_3 \) 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 \( \text{CH}_3\text{ONO} \), NO, \( \text{NO}_2 \), and the organic reaction products, react with these organics:

\[
\text{OH} + \text{reactant} \rightarrow \text{products}
\]

(3)

\[
\text{OH} + \text{reference organic} \rightarrow \text{products}
\]

(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

\[
\frac{-\text{dln}([\text{reactant}])}{\text{dt}} = k_3[\text{OH}]
\]

(III)

and

\[
\frac{-\text{dln}([\text{reference organic}])}{\text{dt}} = k_4[\text{OH}]
\]

(IV)

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

\[
\ln \left( \frac{[\text{reactant}]_t}{[\text{reactant}]_0} \right) = \frac{k_3}{k_4} \ln \left( \frac{[\text{reference organic}]_t}{[\text{reference organic}]_0} \right)
\]

(V)

where \([\text{reactant}]_0\) and \([\text{reference organic}]_0\) are the concentrations of the reactant and reference organic, respectively, at time \( t_0 \), and \([\text{reactant}]_t\) and \([\text{reference organic}]_t\) are the corresponding concentrations at time \( t \). Thus plots of \( \ln([\text{reactant}]_t/[\text{reactant}]_0) \) against \( \ln([\text{reference organic}]_t/[\text{reference organic}]_0) \) should yield straight lines of slope \( k_3/k_4 \) and zero intercept.

For these relative rate measurements irradiations were carried out in an \(~60-\ell\) 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 \( \text{CH}_3\text{ONO} \) 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 quan-
titatively 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 employ-
ed 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 concentra-
tions 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 inter-
ferometer 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$_3$ONO, and NO, with air as the diluent gas. Partial pressures of CH$_3$ONO, 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$_2$ClCH=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$_3$ONO was prepared by dropwise addition of 50% H$_2$SO$_4$ to a saturated solution of NaNO$_2$ in CH$_3$OH 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
\( \ln([O_3]_t / [O_3]_o) \) against time \((t - t_o)\), where \([O_3]_t\) and \([O_3]_o\) 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 \textit{cis}- and \textit{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 \textit{cis}- and \textit{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 \pm 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 \textit{cis} sample did not affect the above results, since this impurity was shown to be unreactive towards \(O_3\) (cf. below).

2. \textbf{Rate Constants for Reaction with Hydroxyl Radicals}

Irradiations of \(CH_3ONO/NO/n\text{-octane/cis- and trans-1,3-dichloropropene/air mixtures}\) were carried out, with the irradiation times ranging from 15-45 min. \(n\text{-Octane}\) 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 \textit{cis}- and \textit{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-ClCH₂CH=CHCl samples with O₃.
Figure II-2. Plot of equation (V) for the reactions of OH radicals with cis- and trans-ClCH₂CH=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-Dichloro-
propene at 295 ± 2 K

<table>
<thead>
<tr>
<th>Reactant</th>
<th>$k_3/k_4^a$</th>
<th>$10^{11} \times k_3$ (cm$^3$ molecule$^{-1}$ sec$^{-1})^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>cis-1,3-Dichloropropene</td>
<td>0.859 ± 0.013</td>
<td>0.774 ± 0.020</td>
</tr>
<tr>
<td>trans-1,3-Dichloropropane</td>
<td>1.45 ± 0.04</td>
<td>1.31 ± 0.05</td>
</tr>
</tbody>
</table>

$^a$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 $(9.01 ± 0.19) \times 10^{-12}$ 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 5800-1 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 (HCHO) and chloroacetalddehyde (ClCH$_2$CHO). Figure II-3A shows the infrared spectrum of the reaction mixture with initial concentrations of 8.99 ppm trans- and 1.79 ppm cis-ClCH$_2$CHO (from the commercial sample) and 5.3 ppm $O_3$ in air after 38 min of reaction. Subtraction of the absorptions of unreacted trans- and cis-ClCH$_2$CHO 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-ClCH₂CH=CHCl and 5.3 ppm O₃.

(B) Product spectrum minus the absorptions of reactants.

(C) Expanded (2X) residual spectrum after subtraction of HC(O)Cl bands; * - probable absorption bands of ClCH₂COOH.
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 (ClCH₂COOH) appears to be a significant product of the dichloropropene-0₃ 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 "a" in the residual spectrum of Figure II-3C. Upper limit estimates from the spectra indicated ~0.2 ClCH₂COOH formed per 1,3-dichloropropene consumed throughout the reaction; ~0.53 ppm of ClCH₂COOH 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 0₃. In agreement with the results of kinetic experiments, Figure II-4 shows that the trans-isomer reacted much faster than the cis-isomer. The 0₃ decay rate was much faster during the initial stage of the reaction (i.e., ≤3 min) with ~1.5 0₃ 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 0₃. 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 H₂O to form HCl, CO, and HCOOH (Hisatsune and Heicklen 1973). In addition to the observed formation of HCl, CO, CO₂, 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-ClCH₂ CH=CHCl, 1.67 ppm trans-ClCH₂ CH=CHCl, 1.93 ppm CH₃CHClCH₂Cl, and 5.47 ppm 0₃.
Figure II-4. Time-concentration profiles of reactants and products from an air mixture of the trans-ClCH₂CH=CHCl sample and O₃.
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 CH₃ONO/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 CH₃ONO/NO photolysis products (CH₃ONO₂, HCHO, HNO₃, and NO₂) 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-CH₂ClCH=CHCl and 10 ppm each of CH₃ONO 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 HCl and 2.22 ppm of ClCH₂CHO. At 15 min into the irradiation, the corresponding yields were 3.22 ppm of HCl and 3.45 ppm of ClCH₂CHO 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-CH₂ClCH=CHCl, 10 ppm CH₃ONO, 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 CH₃CHClCH₂Cl, CH₃OCH₃, CH₃ONO, and NO in one atmosphere of air. The added CH₃OCH₃ 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 CH₃OCH₃ was observed. From the literature value for the OH radical rate constant of CH₃OCH₃ of (3.5 ± 0.35) x 10⁻¹² cm³ molecule⁻¹ sec⁻¹ (Perry et al. 1977a), the above results yield an upper limit OH radical reaction rate constant of ≤ 6 x 10⁻¹³ cm³ 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 ≥ 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 O₂ to form the corresponding chlorine substituted alkylperoxy radicals. In the presence of NO, the peroxo radicals yield the respective alkoxy intermediates plus NO₂. 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 O₂ completes the reaction, forming one molecule each of HCCl and ClCH₂CHO from either mode of OH radical addition.

2. Reactions with Ozone

The product distribution observed in the reaction of O₃ 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 ClCH₂CH=CHCl with the OH radical.
stoichiometries and mechanisms are involved in these reactions, and a
general scheme is presented for the reaction of O₃ with 1,3-dichloro-
propene 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 CO₂, no
other likely decomposition products arising from B have been identified in
the present study.

By analogy with the formation of ClCH₂C(OH)Cl from B, ClCOOH could also
have been formed from C. Its nondetection is attributed to its known
rapid decomposition to CO₂ and HCl at room temperature (Jensen and
Pimentel 1967). Evidence from the study of the reactions of O₃ with the
chloroethylenes (Niki et al. 1982) also suggests that the thermally active
intermediate C undergoes unimolecular dissociation to produce CO, CO₂, 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 k₂ must be rigorously considered to
be upper limits to the actual rate constants, although at the high
[reactant]/[O₃] ratios used (≥100 for cis- and trans-dichloropropene) any
Cl atoms produced would react essentially totally with the reactant
organic, thus minimizing secondary reactions with O₃. Additional detailed
experiments which are required to define the effects of these secondary
reactions in the 1,3-dichloropropene-O₃ system were beyond the scope of
the present investigation. Nevertheless, the major products which have
Figure II-6. General mechanism for the reaction of ClCH₂CH=CHCl with O₃ 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>
<thead>
<tr>
<th>Alkene</th>
<th>Rate constant (in cm$^3$ molecule$^{-1}$ sec$^{-1}$ units)</th>
<th>O$_3^a$</th>
<th>OH$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_2$=CH$_2$</td>
<td>1.8 x 10$^{-18}$</td>
<td>8.5 x 10$^{-12}$</td>
<td></td>
</tr>
<tr>
<td>CH$_2$=CHCl</td>
<td>2.5 x 10$^{-19}$</td>
<td>6.6 x 10$^{-12}$</td>
<td></td>
</tr>
<tr>
<td>CH$_2$=CCl$_2$</td>
<td>3.7 x 10$^{-21}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>cis-CHCl=CHCl</td>
<td>&lt;5 x 10$^{-21}$</td>
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</tr>
<tr>
<td>trans-CHCl=CHCl</td>
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<tr>
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<td>2.4 x 10$^{-12}$</td>
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<tr>
<td>CCl$_2$=CCl$_2$</td>
<td>&lt;2 x 10$^{-23}$</td>
<td>1.7 x 10$^{-13}$</td>
<td></td>
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<tr>
<td>CH$_3$CH=CH$_2$</td>
<td>1.1 x 10$^{-17}$</td>
<td>2.5 x 10$^{-11}$</td>
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<tr>
<td>cis-CH$_2$ClCH=CHCl</td>
<td>1.5 x 10$^{-19c}$</td>
<td>7.7 x 10$^{-12c}$</td>
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<tr>
<td>trans-CH$_2$ClCH=CHCl</td>
<td>6.7 x 10$^{-19c}$</td>
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<tr>
<td>CH$_2$=C(CH$_3$)$_2$</td>
<td>1.2 x 10$^{-17}$</td>
<td>5.1 x 10$^{-11}$</td>
<td></td>
</tr>
<tr>
<td>CH$_2$=C(CH$_2$Cl)$_2$</td>
<td>3.9 x 10$^{-19}$</td>
<td>3.8 x 10$^{-11}$</td>
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</tr>
</tbody>
</table>

$^a$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 O₃ concentration of \( \sim 1 \times 10^{12} \text{ cm}^{-3} \) (~0.04 ppm) (Singh et al. 1978), the half-lives with respect to reaction with O₃ 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 \( \sim 2 \times 10^6 \text{ cm}^{-3} \) (~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 \( \gtrsim 13 \) days is estimated for a 24-hr average OH radical concentration of \( 1 \times 10^6 \text{ cm}^{-3} \). 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 O₃ 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 HCCl, ClCH₂CHO, and ClCH₂COOH. Whereas formyl chloride is known to eventually decompose and hydrolyze to CO, HCl, and HCOOH, the other toxic products chloroacetyldehyde 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 (CH₂=CHCl), trichloroethylene (CHCl=CCl₂) and tetrachloroethylene (CCl₂=CCl₂) 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 O₃ (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

NOₓ-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 ≥290 nm

\[
\text{CH}_2\text{ONO} + h\nu \rightarrow \text{CH}_3\text{O} + \text{NO}
\]

\[
\text{CH}_3\text{O} + \text{O}_2 \rightarrow \text{HCHO} + \text{HO}_2
\]

\[
\text{HO}_2 + \text{NO} \rightarrow \text{OH} + \text{NO}_2
\]

NO was included in the reaction mixtures in order to minimize the formation of O₃ and of NO₃ radicals. The initial concentrations of the CH₃ONO-NO-chloroethene-air mixtures were: CH₃ONO ~10 ppm, NO ~5-10 ppm, chloroethene ~6-13 ppm, with one atmosphere of dry pure matrix air for the experiments in the 3700-λ all-Teflon chamber or of synthetic air (80% N₂ + 20% O₂) for the 5800-λ 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 CH₃ONO-NO-chloroethene-air mixtures were carried out in both the 3700-λ all-Teflon chamber and in the SAPRC 5800-λ 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 CH₃ONO-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$_3$ONO-NO-Vinyl Chloride-Air Mixtures at 298 K and Atmospheric Pressure

<table>
<thead>
<tr>
<th>Chamber</th>
<th>Initial Concentrations (ppm)</th>
<th>-Δ[Vinyl Chloride] (ppm)</th>
<th>HC(0)Cl (ppm)</th>
<th>Obs. Yield (%)</th>
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<tbody>
<tr>
<td>3700-l</td>
<td>CH$_3$ONO 12 NO 8 Vinyl Chloride 12.53</td>
<td>2.06 3.33 4.21 4.77</td>
<td>1.85 2.79 3.25 3.52</td>
<td>90 84 77 74</td>
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<tr>
<td>all-Teflon</td>
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<td></td>
</tr>
<tr>
<td>5800-l</td>
<td>10 NO 5 Vinyl Chloride 9.64</td>
<td>1.09 2.01 2.53 2.87</td>
<td>1.00 1.74 2.10 2.32</td>
<td>92 87 83 81</td>
</tr>
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<tr>
<td>Chamber</td>
<td>Initial Concentrations (ppm)</td>
<td>(-\Delta \text{[Trichloroethene]}) (ppm)</td>
<td>(\text{HC(O)Cl}) (ppm)</td>
<td>Obs. Yield (%)</td>
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<td>-------------</td>
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<td>3700-Å</td>
<td>11 11 8.87</td>
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<td>4.71</td>
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<td></td>
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<td>4.87</td>
<td>0.84</td>
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<td></td>
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<td>5.10</td>
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Table III-3. Experimental Conditions and Data for the Photolysis of CH\textsubscript{3}ONO-NO-Tetrachloroethene-Air Mixtures at 298 K and Atmospheric Pressure

<table>
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<tr>
<th>Chamber</th>
<th>Initial Concentrations (ppm)</th>
<th>(-\Delta\text{[Tetrachloroethene]}) (ppm)</th>
<th>COCl (ppm)</th>
<th>Obs. Yield (%)</th>
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</thead>
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<td>CH\textsubscript{3}ONO</td>
<td>NO</td>
<td>Tetrachloroethene</td>
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<td></td>
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</table>

\(\text{a}\)The pre-irradiation dark decay of tetrachloroethene was \(\leq 1.3\%\) over a 30 min time period.
formyl chloride (HC(O)Cl) from vinyl chloride, formyl chloride and phosgene (COCl₂) 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 CH₃ONO-NO-air irradiations of vinyl chloride and trichloroethene, and of COCl₂ during the CH₃ONO-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-λ all-Teflon chamber having an anomalously low yield. From the data in the 5800-λ 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:

\[
\begin{align*}
\text{OH} & \rightarrow \text{OH} + \\
\text{C} = \text{C} & \rightarrow \text{C} \cdot \text{C} + \\
& \rightarrow \text{O}_2 + \\
\text{R}_1 \text{OH} \cdot \text{O}_2 & \rightarrow \text{NO}_2 + \\
& \rightarrow \text{R}_1 \text{COR}_2 + \text{R}_3 \text{COR}_4 + \text{other products} \\
& \rightarrow \text{O}_2 \\
& \rightarrow \text{R}_1 \text{COR}_2 + \text{HO}_2
\end{align*}
\]
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:

\[
\text{OH} + \text{CH}_2=\text{CHCl} \xrightarrow{\text{O}_2, \text{NO}} \text{HCHO} + \text{HC}(\text{O})\text{Cl} + \text{HO}_2
\]

However, for trichloroethene, the yields of formyl chloride and phosgene, though essentially identical, are only \(\sim 20-25\%\). Hence it is evident that the reaction of OH radicals with trichloroethene leads, \(\sim 75-80\%\) of the time, to products other than these cleavage products observed. An analogous situation occurs in the case of tetrachloroethene, where the observed \(\sim 53\%\) yield of COCl\(_2\) shows that the above discussed reaction scheme leaving to cleavage of the double bond occurs only \(\sim 25\%\) 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 METHYLGLOYXAL FROM THE NO<sub>x</sub>-AIR 
PHOTOXIDATIONS 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<sub>x</sub>-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)

\[ \text{OH} + \text{toluene} \rightarrow \text{H}_2\text{O} + \text{A} \quad (1) \]

(A)

\[ \text{OH} + \text{toluene} \rightarrow \text{OH} + \text{A} \quad (2) \]
The H-atom abstraction route is relatively minor, accounting for \( \sim 8\% \) of the overall reaction for toluene (Atkinson et al. 1983c) and \( \sim 2-4\% \) 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, Atkinson 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)

For toluene the yield of \( o \)-cresol has been determined to be \( 13 \pm 7\% \) (Atkinson et al. 1983c) and, when combined with the \( (o\)-cresol/total cresol) formation ratio of \( \sim 0.8 \) (Kenley et al. 1981), this leads to a total isomeric cresol yield of \( \sim 16 \pm 8\% \). 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 \( \alpha \)-dicarboxyls 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 \(\alpha\)-dicarboxyls 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 \(\text{NO}_x\)-air photooxidations of toluene, \(m\)-xylene and \(p\)-xylene at \(\sim740\) torr of air and \(298 \pm 2\) K.

B. Experimental

The \(\text{NO}_x\)-air photooxidations of toluene, \(m\)-xylene and \(p\)-xylene were carried out in the SAPRC 5800-\(\lambda\) evacuable, Teflon-coated environmental chamber, with radiation being provided by a \(25\ \text{KW}\) 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 \(\sim250-470\ nm\) 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 \(\sim5 \times 10^{11}\ \text{molecule} \ cm^{-3}\) 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 \(\sim5 \times 10^{12}\ \text{molecule} \ cm^{-3}\). However, at the shorter pathlengths used during the irradiations and in the presence of significant concentrations of \(\text{NO}_2\), 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 \(\sim 4 \times 10^{12}\) molecule cm\(^{-3}\) at the pathlength and resolution employed.

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

\[
\text{CH}_3\text{ONO} + \text{hv} \rightarrow \text{CH}_3\text{O} + \text{NO}
\]

\[
\text{CH}_3\text{O} + \text{O}_2 \rightarrow \text{HCHO} + \text{HO}_2
\]

\[
\text{HO}_2 + \text{NO} \rightarrow \text{OH} + \text{NO}_2
\]

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\(_3\)ONO-NO-aromatic hydrocarbon-air mixtures were: CH\(_3\)ONO 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 \times 10^{-3} \text{ sec}^{-1}, and to a biacetyl photolysis rate of (7.47 \pm 0.21) \times 10^{-5} \text{ 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\(_3\)ONO-NO-air irradiations of toluene, \(\text{m}\)-xylene and \(\text{p}\)-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 methyl-glyoxal (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

\[
\text{NO, O}_2 \rightarrow \text{OH} + \text{aromatic} \rightarrow Y \alpha\text{-dicarbonyl} \quad (5)
\]

\[
\text{OH} + \alpha\text{-dicarbonyl} \rightarrow \text{products} \quad (6)
\]

\[
\alpha\text{-dicarbonyl} + \text{hv} \rightarrow \text{products} \quad (7)
\]

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,

\[
[\text{OH}] = \frac{1}{K_5(t_2-t_1)} \ln \left( \frac{[\text{aromatic}]_{t_1}}{[\text{aromatic}]_{t_2}} \right) \quad (I)
\]

where \([\text{OH}]\) 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,

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

\[
Y_{t_1-t_2} \frac{k_5[\text{OH}]}{[k_6-k_5] \text{[OH]} + k_7} \left[ e^{-k_5[\text{OH}](t_2-t_1)} - e^{-(k_6[\text{OH}] + k_7)(t_2-t_1)} \right] \quad (II)
\]
Table IV-1. Experimental Data for the Formation of Glyoxal and Methylglyoxal from the CH$_3$ONO-NO-Air Photooxidations of Toluene

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

$^a$ 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 CH₃ONO-NO-Air Photooxidations of m-Xylene

<table>
<thead>
<tr>
<th>EC Run No.</th>
<th>10⁻¹⁴ x Initial Concentrations (molecule cm⁻³)</th>
<th>10⁻¹³ x Δ[m-xylene] (molecule cm⁻³)</th>
<th>10⁻¹³ x [Glyoxal]a (molecule cm⁻³)</th>
<th>10⁻¹³ x [Methylglyoxal]a (molecule cm⁻³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>939</td>
<td>3.40 1.13 4.21</td>
<td>7.25 0.65 0.68</td>
<td>1.27 1.38</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>9.94 1.03 1.10</td>
<td>1.78 2.00</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>12.10 0.84 0.95</td>
<td>2.42 2.78</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>14.26 1.13 1.28</td>
<td>2.78 3.32</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>15.74 1.34 1.53</td>
<td>3.34 4.03</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>17.02 1.66 1.89</td>
<td>3.36 4.21</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>18.24 1.63 1.92</td>
<td>3.41 4.42</td>
<td></td>
</tr>
<tr>
<td>940</td>
<td>3.39 1.13 4.38</td>
<td>6.84 1.61 1.73</td>
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<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>9.14 2.23 2.48</td>
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<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>10.99 2.83 3.26</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>12.74 2.66 3.24</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>14.40 2.90 3.65</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>16.25 3.84 4.79</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>17.86 3.55 4.72</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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$_3$ONO-NO-Air Photooxidations of p-Xylene

<table>
<thead>
<tr>
<th>EC Run No.</th>
<th>10$^{-14}$ x Initial Concentrations (molecule cm$^{-3}$)</th>
<th>10$^{-13}$ x -$\Delta$[p-Xylene] (molecule cm$^{-3}$)</th>
<th>10$^{-13}$ x [Glyoxal]$^a$ (molecule cm$^{-3}$)</th>
<th>10$^{-13}$ x [Methylglyoxal]$^b$ (molecule cm$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>938</td>
<td>3.38 1.13 4.71</td>
<td>4.90 1.63 1.72</td>
<td>1.08 1.16</td>
<td>7.54 2.04 2.23</td>
</tr>
<tr>
<td>937</td>
<td>3.08 1.17 3.85</td>
<td>16.25 2.86 3.71</td>
<td>2.16 3.27</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ Determined by DOAS.
$^b$ Determined by FT-IR spectroscopy.
$^c$ Corrected for photolysis and reaction with OH radicals (see text).
where \([α\text{-dicarbonyl}]_{t_1}^\text{corr}\) and \([α\text{-dicarbonyl}]_{t_2}^\text{corr}\) are the α-dicarbonyl concentrations observed at times \(t_1\) and \(t_2\), respectively, and \(Y_t_{t_1-t_2}\) 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:

\[
[α\text{-dicarbonyl}]_{t_2}^\text{corr} = [α\text{-dicarbonyl}]_{t_1}^\text{corr} + Y_t_{t_1-t_2} ([aromatic]_{t_2} - [aromatic]_{t_1})
\]  

(III)

where \([α\text{-dicarbonyl}]_{t_1}^\text{corr}\) and \([α\text{-dicarbonyl}]_{t_2}^\text{corr}\) 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 \(1.66 \times 10^{-5}\) sec\(^{-1}\) and \(4.0 \times 10^{-5}\) 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, \([α\text{-dicarbonyl}]_t^\text{corr}/[α\text{-dicarbonyl}]_t\), 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, \([α\text{-dicarbonyl}]_t^\text{corr}\), are plotted against the amounts of aromatic hydrocarbon consumed, \(-Δ[aromatic]\) [i.e., \(([aromatic]_t - [aromatic]_t^0)\)] 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$_3$ONO-NO-air irradiations of toluene, m-xylene and p-xylene.
Table IV-4. Glyoxal and Methylglyoxal Yields from the \( \text{CH}_3\text{ONO-NO-Air} \) Photooxidations of Toluene, \( m \)-Xylene and \( p \)-Xylene at Room Temperature, and Atmospheric Pressure, Together with the Data of Bandow et al. (1983)

<table>
<thead>
<tr>
<th>Aromatic Hydrocarbon</th>
<th>Glyoxal</th>
<th>Methylglyoxal</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Yield(^a)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>This work</td>
<td>Bandow et al. (1983)</td>
</tr>
<tr>
<td>Toluene</td>
<td>0.173 ± 0.029</td>
<td>0.15 ± 0.04</td>
</tr>
<tr>
<td>( m )-Xylene</td>
<td>0.104 ± 0.020</td>
<td>0.13 ± 0.03</td>
</tr>
<tr>
<td>( p )-Xylene</td>
<td>0.200 ± 0.032</td>
<td>0.24 ± 0.02</td>
</tr>
</tbody>
</table>

\(^a\)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 \( \alpha \)-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 methylglyoxal [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 \( \alpha \)-dicarbonyls (together with the corresponding co-products). However, the \( \alpha \)-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 (RO₂) 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 NO₂ and an alkoxy radical (Finlayson-Pitts and Pitts 1977, Atkinson and Lloyd 1984).

\[
RO₂ + NO \rightarrow RO + NO₂
\]

(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.

\[
RO₂ + NO \rightarrow RONO₂
\]

(2)

For the alkyl peroxy radicals generated from the C₂–C₈ n-alkanes, the fraction of the overall reaction forming RONO₂, \(k_2/(k_1 + k_2)\), increases monotonically with the carbon number of the RO₂ 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 NOₓ-air photooxidations of the C₅–C₇ 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 alkyl 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 >290 nm, of methyl nitrite in air at part-per-million concentrations (1 ppm = 2.38 x 10^{13} molecule cm^{-3} at 298 K and 735 torr total pressure)

\[ \text{CH}_3\text{ONO} + \text{hv} \rightarrow \text{CH}_3\text{O} + \text{NO} \]

\[ \text{CH}_3\text{O} + \text{O}_2 \rightarrow \text{HCHO} + \text{HO}_2 \]

\[ \text{HO}_2 + \text{NO} \rightarrow \text{OH} + \text{NO}_2 \]

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-\lambda FEP Teflon cylindrical reaction bag surrounded by 24 GE FL5T8-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/G20M 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$_3$ONO-NO-alkane-air mixtures at >290 nm

\[
\text{CH}_3\text{ONO} + \text{hv} \rightarrow \text{CH}_3\text{O} + \text{NO}
\]

\[
\text{CH}_3\text{O} + \text{O}_2 \rightarrow \text{HCHO} + \text{HO}_2
\]

\[
\text{HO}_2 + \text{NO} \rightarrow \text{OH} + \text{NO}_2
\]

\[
\text{OH} + \text{RH} \rightarrow \text{R}^* + \text{H}_2\text{O}
\]

\[
\text{M} + \text{R} + \text{O}_2 \rightarrow \text{RO}_2
\]

with typical initial reactant concentrations of CH$_3$ONO, ~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$_3$ONO-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$_3$ONO.

In addition to reacting with CH$_3$ONO, NO, NO$_2$ and the organic reaction products, the OH radicals generated from the photolysis of CH$_3$ONO in air can react with the alkyl nitrates and with n-butane

\[
\text{OH} + \text{alkyl nitrate} \rightarrow \text{products} \quad (3)
\]

\[
\text{OH} + \text{n-butane} \rightarrow \text{products} \quad (4)
\]

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)
\[-\frac{\text{dln[alkyl nitrate]}}{\text{d}t} = k_3[\text{OH}] \quad (I)\]

and

\[-\frac{\text{dln[n-butane]}}{\text{d}t} = k_4[\text{OH}] \quad (II)\]

Hence

\[
\text{ln}\left(\frac{[\text{alkyl nitrate}]_t}{[\text{alkyl nitrate}]_o}\right) = k_3 \int_{t_o}^{t} [\text{OH}] \text{d}t \quad (III)\]

\[
\text{ln}\left(\frac{[\text{n-butane}]_t}{[\text{n-butane}]_o}\right) = k_4 \int_{t_o}^{t} [\text{OH}] \text{d}t \quad (IV)\]

and eliminating the OH radical concentration leads to

\[
\text{ln}\left(\frac{[\text{alkyl nitrate}]_t}{[\text{alkyl nitrate}]_o}\right) = \frac{k_3}{k_4} \text{ln}\left(\frac{[\text{n-butane}]_t}{[\text{n-butane}]_o}\right) \quad (V)\]

where \([\text{alkyl nitrate}]_t\) and \([\text{n-butane}]_t\) are the concentrations of the alkyl nitrate and n-butane, respectively, at time \(t\), \([\text{alkyl nitrate}]_o\) and \([\text{n-butane}]_o\) 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 \(\text{ln([alkyl nitrate]_t/[alkyl nitrate]_o)}\) against \(\text{ln([n-butane]_t/[n-butane]_o)}\) 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 \(2.58 \times 10^{-12}\) 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 $298 \pm 2 \text{ K}$

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

$^a$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 $2.58 \times 10^{-12}$ 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.

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 

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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:

$$k[\text{OH} + \text{CH}_2\text{ONO}_2(\text{CH}_2)] \approx k[\text{OH} + \text{CHONO}_2(\text{R})] \approx 0,$$

$$k[\text{OH} + \text{CH}_3(\text{CHONO}_2)] \approx 0.09,$$

and

$$k[\text{OH} + \text{CH}_2(\text{CHONO}_2)(\text{R})] = 0.4$$

where, for example, $\text{CH}_2(\text{CHONO}_2)(\text{R})$ designates a $-\text{CH}_2-$ group bonded to a $>\text{CHONO}_2$ group and an $-\text{R}$ group, where $-\text{R}$ is either a $-\text{CH}_3$ or a $-\text{CH}_2-$ group.

Based on the above group rate constants, and using the $\text{CH}_3(\text{CH}_2)$ and $\text{CH}_2(\text{CH}_3)(X)$ [where $X \equiv \text{CH}_2$, 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 $5.7 \times 10^{-13}$ cm$^3$ molecule$^{-1}$ sec$^{-1}$ and $4.6 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ sec$^{-1}$, respectively, can be estimated. These estimated values are somewhat lower and higher, respectively (by a factor of $\approx 1.4$) 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:

$$k[\text{OH} + \text{CH(CH}_3)_2(\text{CHONO}_2)] = 1.3 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$$

and

$$k[\text{OH} + \text{CH(CH}_3)(\text{CH}_2)(\text{CHONO}_2)] = 1.1 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$$

Assuming that

$$k[\text{OH} + \text{CH}_3(\text{CONO}_2)] \approx k[\text{OH} + \text{CH}_3(\text{CHONO}_2)] = 0.09 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1},$$

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

$$k[\text{OH} + \text{CH}_2(\text{CH}_2)(\text{CONO}_2)] = 0.2 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$$
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 \( \sim 7 \times 10^{-13} \), \( \sim 2.2 \times 10^{-12} \) and \( \sim 3.0 \times 10^{-12} \) 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

\[
\frac{d[RH]}{dt} = -k_5[OH][RH] \quad (VI)
\]

\[
\frac{d[RONO_2]}{dt} = \alpha k_5[OH][RH] - k_3[OH][RONO_2] \quad (VII)
\]

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 \( \alpha \) are the yields of the alkyl nitrates. Under conditions where the OH radical concentration is constant, these equations can be integrated to obtain

\[
[RH]_t = [RH]_0 e^{-k_5[OH]t} \quad (VIII)
\]

and

\[
[RONO]_t = [RH]_0 \frac{\alpha k_5}{(k_5-k_3)} \left[ e^{-k_5[OH]t} - e^{-k_3[OH]t} \right] \quad (IX)
\]
<table>
<thead>
<tr>
<th>Alkane</th>
<th>Initial Conc (ppb)</th>
<th>$-\Delta$[alkane] ppb</th>
<th>Alkyl Nitrate Yields (ppb)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neopentane</td>
<td></td>
<td></td>
<td>Neopentyl nitrate</td>
</tr>
<tr>
<td></td>
<td>CH$_3$ONO NO Alkane</td>
<td></td>
<td>Obs</td>
</tr>
<tr>
<td>~1320</td>
<td>~1000 967</td>
<td>27</td>
<td>1.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>46</td>
<td>2.4</td>
</tr>
<tr>
<td></td>
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<td>60</td>
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<td>74</td>
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<td>88</td>
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<td>Cyclohexane</td>
<td></td>
<td></td>
<td>Cyclohexyl nitrate</td>
</tr>
<tr>
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<td></td>
<td></td>
<td>Obs</td>
</tr>
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<td>Alkane</td>
<td>Initial Conc (ppb)</td>
<td>Δ[alkane] ppb</td>
<td>Alkyl Nitrate Yields (ppb)</td>
</tr>
<tr>
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<td>--------------------</td>
<td>---------------</td>
<td>-----------------------------</td>
</tr>
<tr>
<td></td>
<td>CH₃ONO</td>
<td>NO</td>
<td>Alkane</td>
</tr>
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<td></td>
</tr>
<tr>
<td>2-Methylbutane</td>
<td>~1360</td>
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</tr>
<tr>
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<td>~1220</td>
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<td>2-Methylpentane</td>
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<td>905</td>
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<tr>
<td></td>
<td>~1200</td>
<td>~1000</td>
<td>905</td>
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</tbody>
</table>

continued
Table V-2 (continued) - 3

<table>
<thead>
<tr>
<th>Alkane</th>
<th>Initial Conc (ppb)</th>
<th>-Δ[alkane] ppb</th>
<th>Alkyl Nitrate Yields (ppb)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CH₃ONO NO Alkane</td>
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<td></td>
</tr>
<tr>
<td>3-Methylpentane</td>
<td>~1240 ~1000 879</td>
<td>175 10.4</td>
<td>2-Nitro-3-methylpentane</td>
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<td>246 15.4</td>
<td>Obs 11.0</td>
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<td>281 17.2</td>
<td>Corr 16.9</td>
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<td>303 18.4</td>
<td></td>
</tr>
<tr>
<td></td>
<td>~1320 ~1000 938</td>
<td>190 10.1</td>
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<td>270 15.7</td>
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<td>348 18.1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>~950 ~10,000 955</td>
<td>37 2.0</td>
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</tr>
<tr>
<td></td>
<td></td>
<td>67 3.5</td>
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</tr>
<tr>
<td></td>
<td></td>
<td>100 4.1</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>130 6.3</td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) Corrected using the OH radical rate constant determined in this work.
\(^b\) Tentative assignment. OH radical rate constant estimated to be \(~7 \times 10^{-13}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{sec}^{-1}\).  
\(^c\) Tentative assignments. OH radical rate constants estimated to be \(~2.2 \times 10^{-12}\) and \(~3.0 \times 10^{-12}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{sec}^{-1}\), respectively.
where $[\text{RH}]_0$ is the initial alkane concentration, $[\text{OH}]$ is the constant hydroxyl radical concentration, and $[\text{RH}]_t$ and $[\text{RONO}_2]_t$ are the alkane and alkyl nitrate concentrations, respectively, at time $t$. Equations (VIII) and (IX) can be combined to obtain

$$\alpha = F \left( \frac{[\text{RONO}_2]_t}{\Delta[\text{RH}]_t} \right)$$

(X)

where

$$F = \left( \frac{k_5 - k_3}{k_5} \right) \left[ \frac{1 - \frac{[\text{RH}]_t}{[\text{RH}]_0}}{\left( \frac{[\text{RH}]_t}{[\text{RH}]_0} \right) \frac{k_3}{k_5} - \left( \frac{[\text{RH}]_t}{[\text{RH}]_0} \right)} \right]$$

(XI)

and $\Delta[\text{RH}]_t = ([\text{RH}]_0 - [\text{RH}]_t)$. 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 $[\text{OH}]$ 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$_3$ONO-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

<table>
<thead>
<tr>
<th>Alkane</th>
<th>Alkyl Nitrates</th>
<th>Yield $^a$</th>
<th>% RO$_2$ Formed</th>
<th>$k_2/(k_1 + k_2)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neopentane</td>
<td>Neopentyl nitrate</td>
<td>0.0513 ± 0.0053</td>
<td>100</td>
<td>0.0513 ± 0.0053</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>Cyclohexyl nitrate</td>
<td>0.160 ± 0.015</td>
<td>100</td>
<td>0.160 ± 0.015</td>
</tr>
<tr>
<td>2-Methylbutane</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>3-Nitro-2-methylbutane</td>
<td>0.0381 ± 0.0009</td>
<td>35</td>
<td>0.109 ± 0.003</td>
</tr>
<tr>
<td></td>
<td>2-Nitro-2-methylbutane$^c$</td>
<td>0.0277 ± 0.0011</td>
<td>52</td>
<td>0.0533 ± 0.0022</td>
</tr>
<tr>
<td>2-Methylpentane</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2-Nitro-2-methylpentane</td>
<td>0.0133 ± 0.0036</td>
<td>38</td>
<td>0.0350 ± 0.0096</td>
</tr>
<tr>
<td></td>
<td>+4-Nitro-2-methylpentane$^c$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3-Methylpentane</td>
<td>2-Nitro-3-methylpentane</td>
<td>0.0671 ± 0.0064</td>
<td>48</td>
<td>0.140 ± 0.014</td>
</tr>
</tbody>
</table>

$^a$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, propionylaldehyde, 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 ± 3.8%, 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$_3$ONO-NO-alkane-air photolysis system are as follows:

\[
\begin{align*}
\text{CH}_3\text{ONO} + h\nu & \rightarrow \text{CH}_3\text{O} + \text{NO} \\
\text{CH}_3\text{O} + \text{O}_2 & \rightarrow \text{HCHO} + \text{HO}_2 \\
\text{HO}_2 + \text{NO} & \rightarrow \text{OH} + \text{NO}_2 \\
\text{OH} + \text{RH} & \rightarrow \text{R} + \text{H}_2\text{O} & (5) \\
\text{M} & \\
\text{R} + \text{O}_2 & \rightarrow \text{RO}_2 & (6) \\
\text{RO}_2 + \text{NO} & \rightarrow \text{RO} + \text{NO}_2 & (1) \\
\text{M} & \\
\text{M} & \rightarrow \text{RONO}_2 & (2) \\
\text{RO} + \text{NO}_2 & \rightarrow \text{RONO}_2 & (7) \\
\text{O}_2 \text{NO} & \\
\text{RO} & \rightarrow \text{OH} + \text{oxygenated products} & (8) \\
\text{NO}_2 & \\
\text{OH} + \text{RONO}_2 & \rightarrow \text{products} & (3)
\end{align*}
\]

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 (\( \text{NO}_2\text{NO}_2 \)) 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 \( k_1 = 1.5 \times 10^{-11} \) 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 \( 8 \times 10^{-15} \) cm\(^3\) molecule\(^{-1}\) sec\(^{-1}\) at 296 K for the reaction

\[
\text{C}_2\text{H}_2\text{O} + \text{O}_2 \rightarrow \text{CH}_3\text{CHO} + \text{HO}_2
\]

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 \( \sim 1.5 \) 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\(_3\)ONO, 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 (\( > \text{C}_4 \)) 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 correspond-
ing secondary alkoxy radicals with NO$_2$ in the CH$_3$ONO-NO-alkane-air irradiations carried out in this study.

For the two tertiary alkoxy radicals, the decomposition rates for (CH$_3$)$_2$C(0)C$_2$H$_5$ and (CH$_3$)$_2$C(0)C$_3$H$_7$ are $\sim$5 x 10$^4$ sec$^{-1}$ and $>5 \times 10^4$ 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$_3$ONO-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$_3$ONO would have been photolysed 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:
\[
\text{CH}_3 \quad 0_2 \quad \text{CH}_3 \\
\text{OH} + \text{CH}_3\text{CHCH}_2\text{CH}_3 \rightarrow \text{CH}_3\text{CHCH}_2\text{CH}_20_2 \\n4\% \\
\]

\[
0_2 \quad \text{CH}_3 \\
\rightarrow \text{CH}_3\text{CHCHCH}_3 \\n35\% \\
\]

\[
0_2 \quad \text{CH}_3 \\
\rightarrow \text{CH}_3\text{CCH}_2\text{CH}_3 \\n52\% \\
\]

\[
0_2 \quad \text{CH}_20_2 \\
\rightarrow \text{CH}_3\text{CHCH}_2\text{CH}_3 \\n9\% \\
\]

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 \(\text{C}_2-\text{C}_8\) \(n\)-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 \(\text{RO}_2\) radical (from \(\sim 0.04\) for \(\text{C}_3\) to \(\sim 0.33\) for \(\text{C}_8\)), 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 \(\text{C}_6\) 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 \(\text{C}_6\) 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>
<thead>
<tr>
<th>Alkane</th>
<th>Primary</th>
<th>Secondary</th>
<th>Tertiary</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>RO₂</td>
<td>k₂/(k₁ + k₂)</td>
<td>RO₂</td>
</tr>
<tr>
<td>Ethane</td>
<td>ethyl</td>
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</tr>
<tr>
<td>Propane,a</td>
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<td>0.020 ± 0.009</td>
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<td>≤0.040</td>
<td>2-butyl</td>
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<tr>
<td>n-Pentane,a,b</td>
<td>-</td>
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<td>2-pentyl</td>
</tr>
<tr>
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<td></td>
<td></td>
<td>3-pentyl</td>
</tr>
<tr>
<td>Neopentane</td>
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<td>0.0513 ± 0.0053</td>
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<td>2-Methylbutane</td>
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<td>2-methyl-3-butyl</td>
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<td>n-Hexane,a</td>
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<tr>
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<td>3-methyl-2-pentyl</td>
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</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>4-octyl</td>
</tr>
</tbody>
</table>

*aCalculated from the data of Atkinson et al. (1982a).
*bCalculated 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 C₅ 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 RO₂ radicals with NO, an important input into the chemical computer sub-models of trajectory or grid airshed models.
VI. REFERENCES


VI-1


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


VI-3


