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**ATMOSPHERIC CHEMISTRY OF VOLATILE  
ORGANIC COMPOUNDS**

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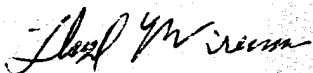
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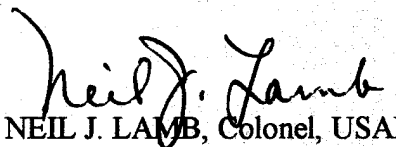
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<b>14. Abstract</b> The relative hydroxyl (OH) reaction rates from the simulated atmospheric oxidation of several alkenes, acetates and other oxygenated organic compounds have been measured. The OH radical was generated from the photolysis of methyl nitrite in air. The reaction products of 2-ethoxyethyl acetate with OH are identified and quantified and a reaction mechanism is proposed. The measured rate constants ( $\times 10^{(-11)}\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$ ) are: $6.77 \pm 0.50$ for trans-4-octene, $1.40 \pm 0.07$ for 4-methyl-2-pentanone, $6.70 \pm 0.23$ for trans-2-heptene, $.342 \pm 0.087$ for n-propyl acetate, $.571 \pm 0.094$ for n-butyl acetate, $0.753 \pm 0.048$ for n-pentyl acetate, $1.056 \pm 0.131$ for 2-ethoxyethyl acetate, $1.356 \pm 0.232$ for 2-ethoxyethyl isobutyrate, $2.722 \pm .206$ for 2-ethoxyethyl methacrylate, $4.34 \pm 0.385$ 4-penten-1-yl acetate, and $3.33 \pm 0.122$ for 3-ethoxyacrylic acid ethyl ester.					
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## **PREFACE**

This report was prepared by ManTech Environmental Technologies, Inc., 2 Triangle Drive, P.O. Box 12313, Research Triangle Park, NC 27709, as part of the requirements of subcontract No. 905A21959-01 under USAF Contract No. F08635-90-C-0048, SETA Task Order Contract for the Armstrong Laboratory, Environics Directorate, Tyndall Air Force Base, FL 32403-5323.

## EXECUTIVE SUMMARY

### A. OBJECTIVE

The objective of this effort was to determine the atmospheric lifetimes, hydroxyl radical rate constants, and possible reaction products of several volatile organic compounds (VOC) or prototypical VOC used by the Air Force in its operations.

### B. BACKGROUND

The Montreal Protocol, the London Amendments, and implementing DoD and Air Force documents specify the removal of chemicals from the inventory that are harmful to the environment. Research is required to understand the full extent of a chemical's impact on the environment. The atmospheric chemistry of these solvents is complex and understanding their atmospheric chemistry builds a knowledge base to interpret future chemicals' atmospheric impact. This research can also signal potentially harmful atmospheric reaction products as well as indicate solvents that are relatively benign. The information produced by this research is useful to help guide the Air Force in selecting the best chemical for the task and the environment.

### C. SCOPE

The following compounds were studied:

- Trans-4-octene
- Trans-2-heptene
- 4-methyl-2-pentanone
- n-propyl acetate
- n-butyl acetate
- n-pentyl acetate
- 2-ethoxyethyl acetate
- 2-ethoxyethyl isobutyrate
- 2-ethoxyethyl methacrylate
- 4-penten-1-yl acetate
- 3-ethoxyacrylic acid ethyl ester
- 2-ethoxy ethanol

During this study, samples of various volatile organic compounds (VOCs) (some of them part of the Air Force chemical inventory) were subjected to OH radical reactions and simulated atmospheric conditions. To accomplish the objectives of this project the following tasks were completed:

1. Construction of a large (3000 liter) Teflon<sup>®</sup> chamber coupled to a Nicolet Fourier Transform infrared (FTIR) spectrometer using a white cell optical path. The white cell gave an

effective absorption path length of approximately 70 meters. This chamber was surrounded by fluorescent lights simulating actinic radiation. The large chamber was also connected to a Hewlett Packard gas chromatograph (GC) so that chamber contents could be analyzed.

2. Fabrication of a small Teflon® chamber (30-100 liter) apparatus that included GC with a flame ionization detector.

3. Fabrication of a special sample loop/injection system to collect chamber contents reproducibly and with high accuracy.

4. Construction of a darkroom with glass gas handling system for the synthesis of the OH radical precursor methyl nitrite, CH<sub>3</sub>ONO.

5. Implementation and acquisition of various analytical instruments for data collection.

6. Fabrication of electronics to control the sample loop temperature precisely for sample collection and injection.

#### D. METHODOLOGY

The atmospheric fate of the target VOC was studied under simulated atmospheric (tropospheric) conditions. OH radicals were generated from photolysis of methyl nitrite, CH<sub>3</sub>ONO in the presence of NO<sub>x</sub>. The relative rate technique was used to measure the OH radical + VOC reaction rate constant. The established reaction rate constant of a reference VOC was used to determine the unknown VOC reaction rate constant. The products of the OH + VOC reaction were monitored by long path Fourier Transform infrared (FTIR) spectroscopy, gas chromatography, mass spectroscopy.

#### E. TEST DESCRIPTION

The VOCs were investigated under simulated atmospheric (tropospheric) conditions. The VOCs were tested for possible photolysis, and OH reaction rate constant. The atmospheric product formation of 2-ethoxyethyl acetate was investigated using gas chromatography/mass spectroscopy/infrared spectroscopy and long path infrared spectroscopy.

#### F. RESULTS

The following summarizes the results from the laboratory investigations:

1. The rate constants of most of the solvents or prototypical solvents tested have very fast OH radical rate constants. The resulting tropospheric half-lives are relatively short and suggest these compounds may contribute significantly to urban ozone episodes when released in the urban atmosphere.

2. The identification of the OH radical + 2 ethoxyethyl acetate reaction products leads to a better understanding of this compound's reaction mechanism.

## G. CONCLUSIONS

Measurements of the hydroxyl radical rate constants of these VOCs are crucial for estimating VOC atmospheric lifetime. The measured reactions rate constant and reaction mechanism information generated by this report can be used by the Air Force and the general public to select appropriate chemicals in the future. The information presented here is also important for atmospheric modelers to determine the global effects of adding these compounds to the hydrocarbon load in the atmosphere.

## H. RECOMMENDATIONS

Development of the analytical methodologies and experimental techniques such as chromatography and mass spectroscopy and infrared spectroscopy continues to aid in the understanding of these very important atmospheric reactions. Work needs to continue as new chemicals are being evaluated by the Air Force and the rest of the Department of Defense. Developing a better understanding of the effect of releasing several different chemicals at once into the atmosphere is a future direction that needs to be investigated. This scenario is actually closer to real-world applications, because the products used are rarely a single compound.

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## SECTION I

### INTRODUCTION

#### A. OBJECTIVE

The objective of this research project is to determine the atmospheric photochemical reactivity of selected volatile organic compounds (VOCs) used by the US Air Force in various operations such as cleaning, degreasing, painting and other solvent usages. This study will include reaction chemical kinetics, reaction mechanisms, and reaction products of the interactions of VOCs with the hydroxyl radical (OH) in the atmosphere. This information will be used to assess the environmental impact of emissions from selected Air Force operations. Vapor recovery and scrubbing devices are costly and the type of scientific information gained from this study will provide a basis for the cost-effective environmental control strategies consistent with federal, state, and local regulations dealing with air quality controls.

#### B. BACKGROUND

Twenty years ago, the first currently accepted chemical mechanisms to explain the formation of photochemical smog were presented. However, even before these were published, it was recognized that the formation of ozone in urban environments resulted through a series of branching chain reactions involving hydrocarbons (HCs) and oxides of nitrogen ( $\text{NO}_x$ ). What was not recognized was the crucial role played by the hydroxyl radical (OH) to initiate the photochemical chain. Chain carriers in these mechanisms also included organic peroxide and alkoxy radicals and the hydroperoxyl radical ( $\text{HO}_2$ ). These branching chain reactions serve to

regenerate OH, and in the process many organic products are formed, including aldehydes and ketones, peroxyacyl nitrates, organic nitrates and peroxides, and other products. During photooxidation nitric oxide (NO) is converted to nitrogen dioxide (NO<sub>2</sub>) which then photolyses to produce ozone (O<sub>3</sub>).

In urban environments, oxides of nitrogen (particularly NO) required for these reactions to occur come primarily from automobile exhaust, although other industrial sources can contribute. On the other hand, sources of hydrocarbons which contribute to the atmospheric load are varied and numerous and include automobile emissions, industrial emissions, other fossil fuel combustion, commercial emissions, household use of cleaning agents and solvents, natural emissions, and other sources. Evaluating the contribution of each of these sources to the total hydrocarbon loading in a particular regional area is difficult and, in fact, is only beginning to be addressed by the U.S. Environmental Protection Agency. Since much of the volatile organic emissions loading can come from numerous small sources, it has become imperative for local and state governments to regulate many generators of volatile organic emissions.

The US Air Force in the course of its normal, peacetime operations performs many regular activities which result in emission of volatile organic compounds (VOCs). A common maintenance operation is the stripping and repainting of aircraft. This process requires large quantities of organic solvents that evaporate into the atmosphere. The Department of Defense (DoD) has committed itself to complying with local and state regulation, therefore, the impact of these evaporated solvents must be evaluated. In addition, there is a need for understanding the fundamental effects a VOC has on a local region as well as globally. These effects can be considered by the following series of questions: (1) What is the atmospheric lifetime of the

emitted VOC; (2) What are the identities and yields of the products formed during the atmospheric degradation of the VOC; and (3) Is the VOC effective in producing ozone when oxidized in the presence of  $\text{NO}_x$ ? The answer to these questions is ultimately grounded in understanding the gas-phase kinetics and mechanisms of these compounds when photooxidized under atmospheric conditions.

These solvents or VOCs can interact with trace chemical species such as OH and  $\text{NO}_3$  in the atmosphere. These reactions generate products that can further react generating a host of other chemical species. This series of reactions has been shown to eventually produce ozone and a variety of oxygenated and nitrogenated organic species [1]. Therefore research on the solvents and their interaction with the atmosphere is very useful to determine the environmental impact of a maintenance operation. For the program described in this report, selected VOCs were studied in order to determine their OH rate constants and the products of the atmospheric reactions.

### C. SCOPE/APPROACH

In general, kinetic studies are concerned only with the rate of removal of chemical species. Mechanistic studies, on the other hand, are concerned with the identity and yield of products generated during the photochemical degradation. However, once the kinetic studies have been completed, as is often the case, a single process is responsible for a large fraction of the total atmospheric removal. Thus, mechanistic studies are frequently focussed on the reactions of a single radical (or photolysis). Removal by the hydroxyl (OH) radical is the predominant path for atmospheric removal of many VOC, thus most mechanistic studies focus on products generated from reaction by OH.

A number of methods have been used over the years to obtain product information from elementary chemical reactions. These have included both spectroscopic and chromatographic methods. The most frequently used methods for product identification have been gas chromatography/mass spectroscopy (GC/MS) and Fourier transform infrared spectroscopy (FTIR). GC/MS has the advantage of being highly specific with a vast library of identified spectra available. However, this technique involves passing the sample through a chromatographic column. Many labile species formed in these photooxidation reactions either cannot be chromatographically separated or give poor peak shapes and chromatographic sensitivities. FTIR has been used successfully over a number of years to identify gas-phase products *in situ* in a smog chamber during the course of an irradiation. Problems related to losses during sampling are thus by passed using this technique. However, this technique measures the presence of all compounds in the system, reactants and products. If this technique is to be viable, a careful spectral subtraction is frequently required to identify and quantify the relatively low concentration

product peaks. This technique has proved to be valuable in discovering new reaction paths for the degradation of VOCs.

As discussed in the background section, there are three general areas for study to evaluate the disposition of emitted VOCs: (1) The reaction rate of VOC + OH, ozone ( $O_3$ ), and  $NO_3$ , and photolysis; (2) Identification of the mechanistic pathways and product yields; and 3) The overall potential for the VOC to form ozone under atmospheric conditions. Numerous studies have examined each of these aspects from a wide array of VOCs, although not all aspects have been considered for each compound studied.

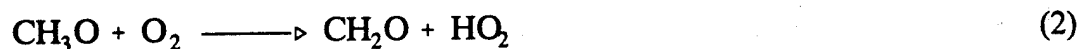
Target compounds include major VOCs used at U.S. Air Force cleaning and painting facilities. These compounds are all oxygenated and can be classified as alcohols, esters, or ketones. Several of these have had only a single study and virtually no product information has been generated.

## SECTION II

### EXPERIMENTAL

#### A. HYDROXYL RADICAL GENERATION

Hydroxyl radicals were generated in Teflon<sup>®</sup>-film bags by the photolysis of methyl nitrite in air [1].



The methyl nitrite was synthesized by dropwise addition of 50% sulfuric acid into a methanol-saturated solution of sodium nitrite developed by Taylor *et al.* [2]. The purity of the methyl nitrite was confirmed by GC/MS and FTIR analysis and stored in the dark at 193 K or collected in a lecture bottle and stored at room temperature.

For the OH kinetic experiments, irradiations were carried out in 30- to 100-liter, 2-mil FEP Teflon<sup>®</sup> surrounded by mixtures of black (UV) and actinic lights. The experimental apparatus is diagrammed in Figure 1. The mixture typically consisted of six 40-watt black lights (GE F40 TB BLB) and four 40-watt sun lights (Westinghouse F40). These light bank mixtures produced 300-450 nm photons. The bag and lamps were housed inside an aluminum box with a fan to maintain a constant temperature inside the bag.

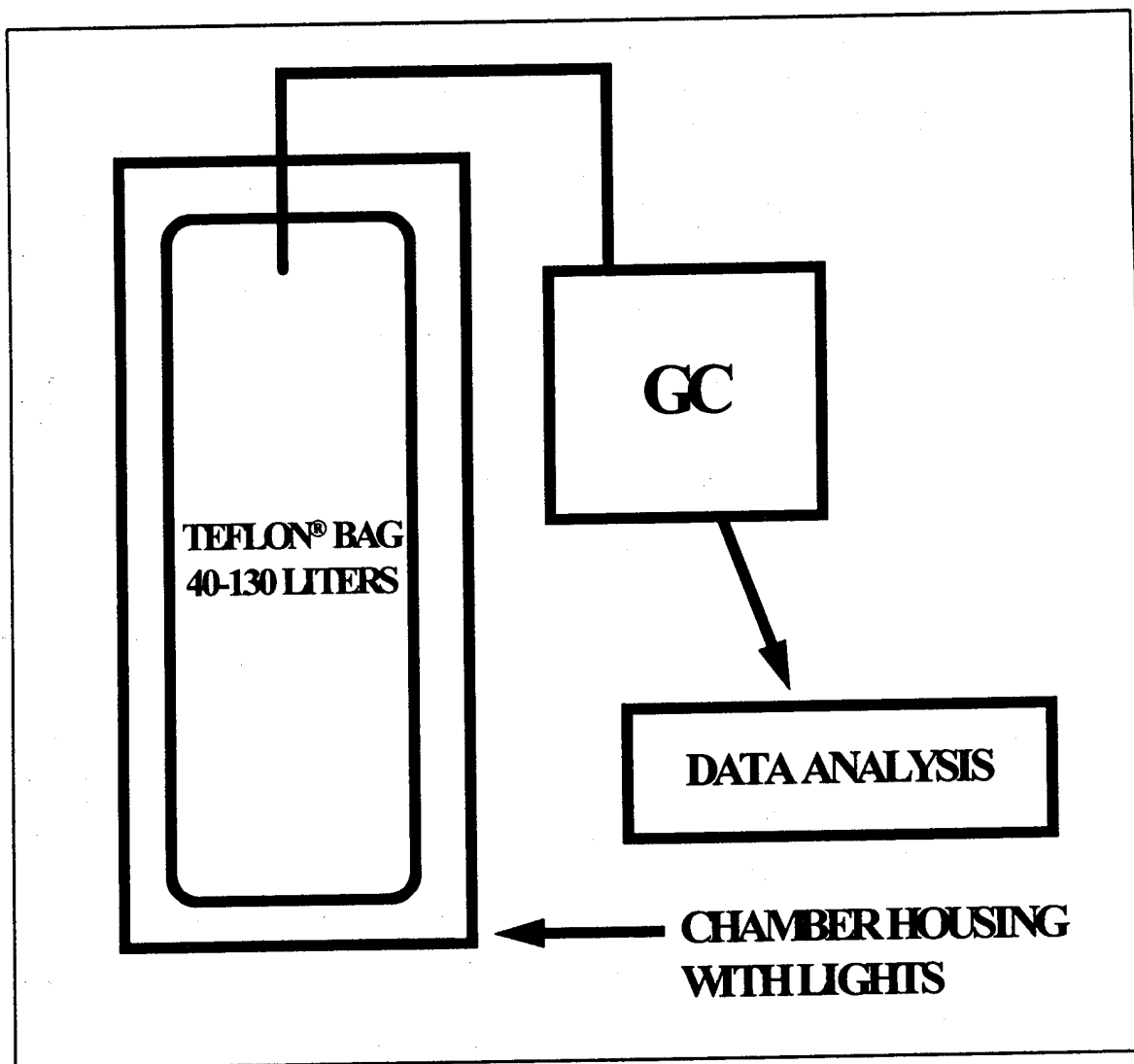


Figure 1. The small chamber apparatus. Data analysis consists of computer collection of flame ionization detector signal.

The 4-Methyl-2-pentanone, *trans*-4-octene, and *trans*-2-heptene (Aldrich Chemical Co.) were 99% pure. *N*-propyl acetate, *n*-butyl acetate, *n*-pentyl acetate, 2-ethoxyethyl acetate, 2-ethoxy ethanol, 2-ethoxyethyl isobutyrate, 2-ethoxyethyl methacrylate, 4-penten-1-yl acetate, 3-ethoxyacrylic acid ethyl ester (Aldrich Chemical Co.) were 99% pure. Purity was confirmed by GC analysis. Nitric oxide (100 ppm in nitrogen, Matheson Co.) was used as received. Propene (M.G. Industries), the principal reference compound, *trans*-2-butene (Matheson Co.) and *n*-butane (Matheson Co.) were research grade. Hexane and heptane (Aldrich, 99+%) were used as received.

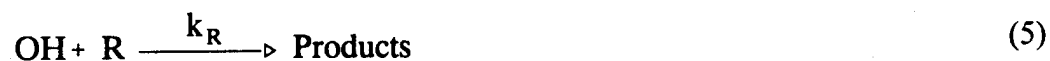
The following chromatographic columns were used during this research : Restek RTx<sup>®</sup>-35, 30 m, 0.53 mm ID; Supelco SPB<sup>®</sup>-5, 15 m, 0.53 mm ID; Supelco SPB<sup>®</sup>-10, 15 m, 0.53 mm ID; Supelco SPB<sup>®</sup>-20, 30 m, 0.32 mm ID.

## B. RELATIVE RATE TECHNIQUE

The relative rate technique was used to measure OH rate constants for the compounds of interest listed above [1]. The experiment consists of placing the compound of interest (the sample S), a reference compound (R), an OH radical source, and an excess of NO into a Teflon<sup>®</sup> bag (Figure 1). This mixture is then irradiated for specific time intervals. After each irradiation a portion of contents (50-300 mL) from the Teflon<sup>®</sup> chamber is collected onto a cryogenically cooled sample loop then flash heated. The sample is launched onto the gas chromatographic column and analyzed by gas chromatography. The concentrations of the reference and the sample compound are used to determine the OH rate constant for the sample compound.

The OH radicals generated by the photolysis of CH<sub>3</sub>ONO react with reference,

R, and sample, S, :



Assuming that the reaction with OH is the only significant loss process for both the reference and sample, the rate equations for reactions (4) and (5) are combined and integrated resulting in the following equation:

$$\ln \frac{[\text{S}]_0}{[\text{S}]_t} = \frac{k_S}{k_R} \ln \frac{[\text{R}]_0}{[\text{R}]_t} \quad (6)$$

Where  $[\text{X}]_0$  refers to the species concentration before OH radical generation and  $[\text{X}]_t$  refers to species concentration at some arbitrary reaction time,  $t$ . Plots of  $\ln([\text{S}]_0/[\text{S}]_t)$  versus  $\ln([\text{R}]_0/[\text{R}]_t)$  are linear with a slope of  $k_S/k_R$  and an intercept of zero. This is shown in Figures 3 through 11. Therefore, multiplying the slope of the linear least squares fit of the data by the established rate constant,  $k_R$ , yields  $k_S$ .

$$k_S = k_R \times \text{slope} \quad (7)$$

## C. EXPERIMENTAL PARAMETERS

### 1. OH Rate Constant Experiments

The reaction vessel (30- to 100-liter Teflon® bag) and the irradiation lights were housed in an aluminum box with a fan to maintain ambient temperature inside the box (Figure 1). The primary photodissociation rate constant for nitrogen dioxide (NO<sub>2</sub>), reaction 8, was used as a measure of the lamp intensity (UV flux) inside the aluminum box [3-5]. The actinometric determination of the rate constant  $k_{\text{NO}_2}$  was based on the photolysis of NO<sub>2</sub> in nitrogen at one



atmosphere. The average value for  $k_{\text{NO}_2}$  was about 0.2 min<sup>-1</sup>.

Reaction mixtures consisted of a reference compound (1 to 3 ppmv), sample compound (1 to 5 ppmv), methyl nitrite (0.5 to 20 ppmv as the OH source), nitric oxide (NO) (1 to 4 ppmv added to support the chain reaction and suppress ozone reactions). These components, except methyl nitrite and NO, were added to the air stream flowing into the bag. Oxides of nitrogen (NO<sub>x</sub>) were measured with a Monitor Labs 8841. Methyl nitrite was collected and transported in the dark in a gas tight syringe and directly injected into the bag that was stored in the dark. The contents mixed for 30 minutes to 4 hours and prephotolysis reactant concentrations ( $[\text{S}]_0$  and  $[\text{R}]_0$ ) were measured. Approximately 50 to 200 milliliters of the chamber contents were sampled by vacuum collection onto a glass-bead-filled sample loop (approximate volume 1.3 mL) cryogenically cooled to a specified temperature, typically -180°C, then flash-heated and injected onto a megabore or capillary gas chromatographic column. The reactant concentrations were monitored by gas chromatography (Hewlett-Packard Model 5890 GC) with flame ionization detection (FID), using a fused-silica megabore column (Restek RTx®-35, 30 m, 0.53 mm ID;

Supelco SPB®-5, 15 m, 0.53 mm ID; Supelco SPB®-10, 15 m, 0.53 mm ID; Supelco SPB®-20, 30 m, 0.32 mm ID). Typically, the GC oven temperature was programmed from 35 to 210°C with helium as the carrier gas.

The key assumption of the relative rate technique is the decrease of both the reference and the sample concentration is due solely to reaction with photolytically generated the hydroxyl radical. Typical experimental mixtures of methyl nitrite, sample and reference were left in the dark for an average experimental period (up to eight hours). In all cases there was no observable loss of components. The reference compound and the sample compound were exposed to several hours of chamber lights. In all cases no detectable loss of reference or sample was observed. These experiments verified that the reference and sample compounds were not photolyzed by the lights used in the experiments.

Separate experiments in which mixtures of methyl nitrite, NO, and sample or reference were irradiated demonstrated that the primary and secondary reaction products did not overlap with the sample or reference gas chromatograph retention times. The irradiation times for these experiments were longer than a typical experimental run. Maximum irradiation times for all experimental runs was 240 s with an initial 30 s followed by others at 15 to 30 s increments. The total irradiation time was kept as short as possible to prevent complications from the reaction products. Each experiment consisted of 5 to 8 irradiations. The total loss of the sample and reference compounds was usually under 35%.

The Teflon® bag was cleaned at the end of each run by adding 1 to 2 ppm NO and irradiating while evacuating the bag. The bag was then filled with air, a sample was collected and analyzed for trace organic chemicals by gas chromatography with flame ionization detection.

## 2. Product determination

### a. Gas chromatography/mass spectrometry/infrared spectroscopy

Identifying and quantifying the products formed in the hydroxyl radical + volatile organic compound reaction are necessary to better understand the atmospheric reaction mechanisms. Understanding the reaction mechanism gives a better predictive tool for estimating the atmospheric fate of other new Air Force solvents, fuels, and chemicals. Product identification is also necessary to evaluate the environmental impact of the VOC. The reaction products could be more harmful than the compound of interest.

Product identifications were performed using a large reaction chamber (3000-liter) shown in Figure 2 coupled to a Hewlett-Packard (HP) 5890 II Plus GC equipped with an HP 5965 B infrared detector (IRD) and an HP 5971 mass selective detector (MSD). The column effluent was split between the HP 5971 and HP 5965 B using a glass capillary "Y" splitter (Restek Corp., Supelco). This afforded the simultaneous mass spectrum detection and infrared spectrum collection of analyte peaks. The IRD collected an IR spectrum every 0.67 seconds ( $8\text{ cm}^{-1}$  resolution with each four scans (1.5 scans/second) averaged). The MSD collected data in the scan mode and collecting 1.9 scans/second.

A 3,000-liter Teflon<sup>®</sup> chamber (Figure 2) was constructed for the product identification experiments. UV lights of the same type for the small chamber experiments were used to irradiate the chamber contents. Long path infrared mirrors were placed inside the chamber in a conventional white cell arrangement [6]. This allowed for the collection of infrared spectra of the *entire* chamber contents during the course of the reaction. A Nicolet 740 Fourier Transform Infrared (FTIR) spectrometer was used in these experiments. The infrared signature of the

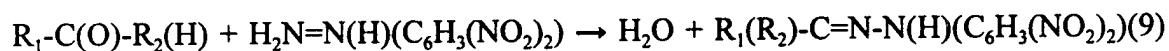
chamber contents contains information indicating the loss of sample and growth of the infrared absorbing products. The major advantage of this collection is the measurement of carbon monoxide (CO) production.

Approximately 50 to 400 mL of the chamber contents were sampled by vacuum collection onto a glass bead filled sample loop (approximate volume 1.3 mL) cryogenically cooled to a specified temperature, typically  $-180^{\circ}\text{C}$ , then flash-heated and injected onto a megabore or capillary gas chromatographic column. Helium was used as the carrier gas and the GC oven temperature was ramped from 35 to  $220^{\circ}\text{C}$ .

The chamber was filled with air, NO (2 to 5 ppm), methyl nitrite (2 to 5 ppm) and the volatile organic compound of interest (5 to 20 ppm). The contents were irradiated initiating Reactions (1), (2), and (3). The OH reacted with the volatile organic compound initiating the reaction chain ultimately leading to products. The chamber contents were analyzed before irradiation to collect a background spectrum. The chamber contents were analyzed after each subsequent irradiation, typically one to five minutes of irradiation.

#### b. Aldehydes and Ketones

The aldehydes and ketones have similar infrared signatures and are therefore difficult to quantify by FTIR. An analytical method by which these aldehydes and ketones are reacted with 1,2 dinitrophenylhydrazine to produce hydrazones (shown below) with subsequent analysis by high pressure liquid chromatography (HPLC) has been a successful technique [7-15].



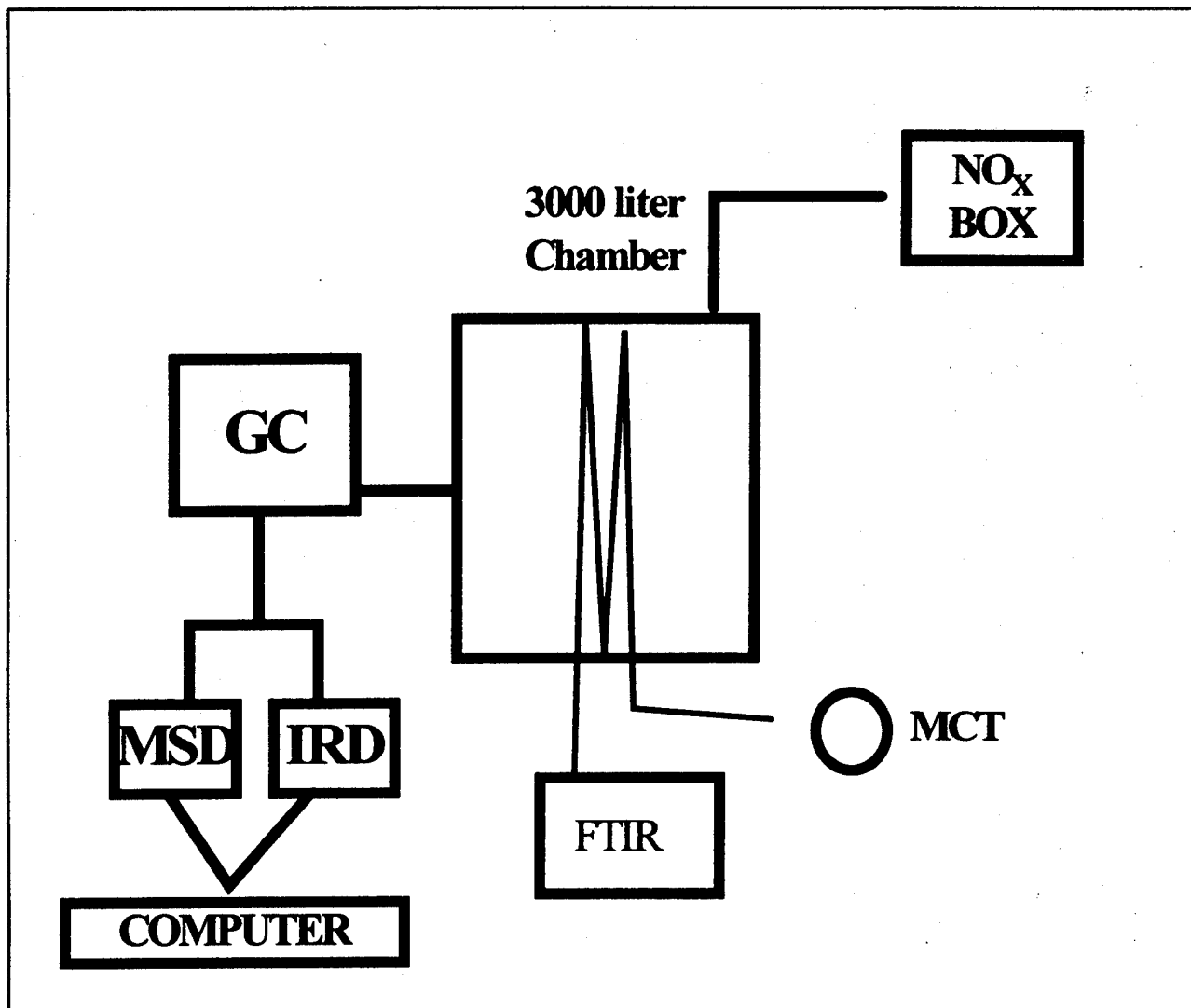


Figure 2. Schematic of the large chamber apparatus. Abbreviations are explained in the text except MCT which is mercury cadmium telluride infrared detector.

The experimental parameters are explained fully in Reference 14. However, a brief description will be provided here.

An HP 1050 HPLC was used with a single DuPont Zorbax™ ODS column (25 cm x 46 cm, 5 μm particle size). Methanol and acetonitrile, both HPLC grade, were obtained from Fisher Scientific and used as received. Water was deionized (18 megohm) using a Milli-Q® system. A 26 minute ternary gradient mobile phase at a constant flow-rate of 1 ml/min was used as follows:

*Water* - 40% decreased linearly to 25% at 10 minutes, further decreased to 15% at 20 minutes and then held constant to 26 minutes.

*Acetonitrile* - 20% decreased linearly to 5% at 10 minutes and then held constant to 26 minutes.

*Methanol* - 40% increased linearly to 70% at 10 minutes, further increasing linearly to 80% at 20 minutes and then held constant to 26 minutes.

### c. Quantification

Quantification data are used to account for the loss of the sample due to OH reaction. This information is used to more clearly describe the reaction mechanism. After the products were identified, an experimental method was developed to determine product rate formation. The sample was placed in the Teflon® bag along with methyl nitrite, NO and air. The mixture was irradiated and the bag contents were sampled with analysis by GC with FID. All of the equipment parameters used for the kinetics experiments were used in these experiments. The product and reactant peaks were calibrated for FID response and those factors were used to determine the concentration of each component in the bag. Decrease of the sample concentration

was monitored as well as the rise of the products' concentrations. A plot of loss of compound of interest versus product formation was linear.

### SECTION III

#### RESULTS

##### A. OH RATE CONSTANTS

Typical plots of  $\ln [S_0]/[S_t]$  versus  $\ln [R_0]/[R_t]$  are shown in Figures 3-11. These results and the chemical structure of the VOC are in Table 1. These are overlay plots for five runs for each sample/reference pair. The slopes of the fitted lines give the rate constant ratios  $k_S/k_R$  as in equation 7. The  $2\sigma$  error limits reported are based on averaging the five slopes for each sample/reference pair plot. The propene reference rate constant of  $2.63 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  was calculated from the Arrhenius expression [16,17]. The rate constant for trans-2-butene by the same procedure was  $6.4 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . These reference OH rate constants were used to determine the OH rate constants for trans-4-octene, trans-2-heptene, and 4-methyl-2-pentanone.

### Trans-2-Heptene OH rate constant w/ Propene

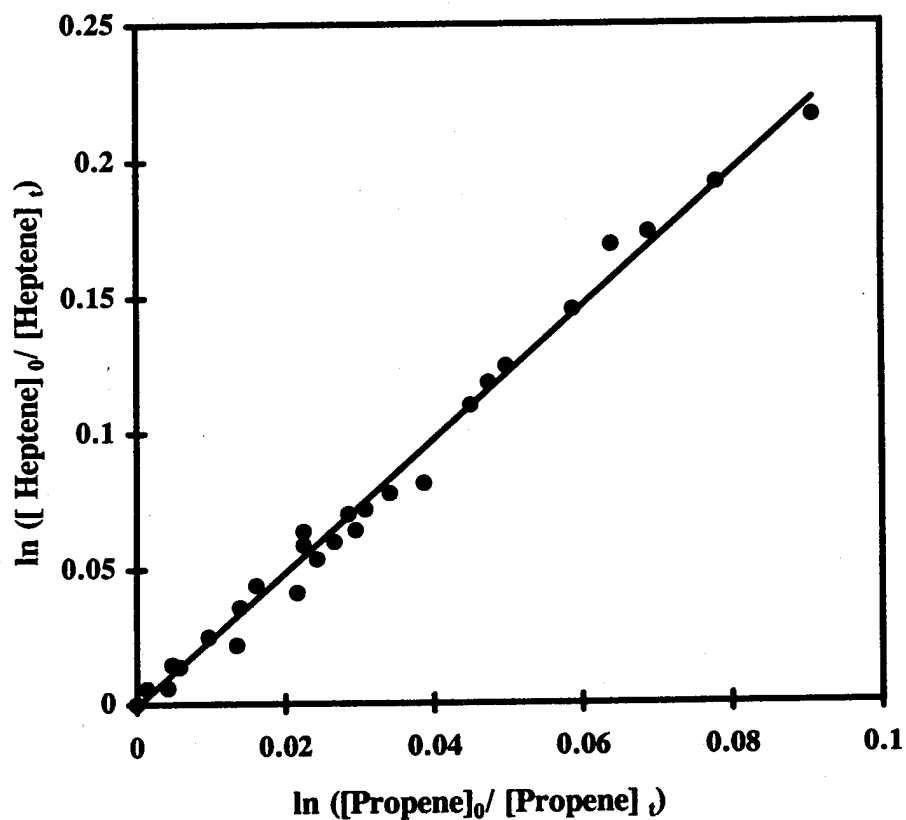


Figure 3. Trans-2-heptene relative plot with propene as the reference compound. This is an overlay of five experiments. The trans-2-heptene rate constant measured is  $6.70 \pm 0.23 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .

**Trans-4-Octene OH rate constant w/  
Propene**

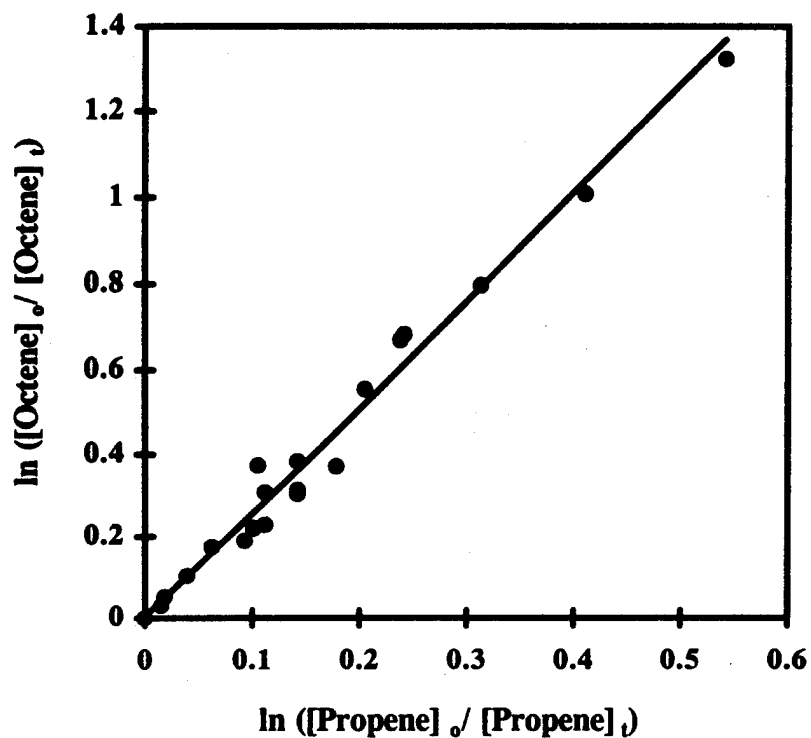


Figure 4. Trans-4-octene relative plot with propene as the reference compound. This is an overlay of five experiments. The trans-4-octene rate constant measured is  $6.77 \pm 0.50 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .

2 Ethoxyethyl acetate OH rate constant w/ Propene

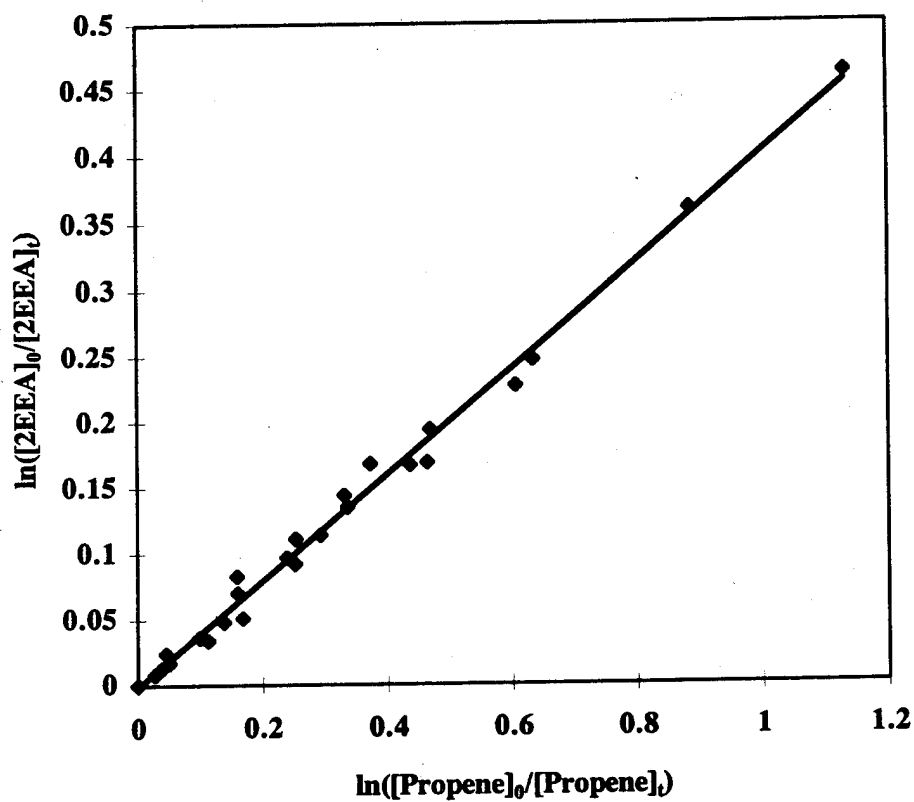


Figure 5. 2-Ethoxyethyl acetate relative plot with propene as the reference compound. This is an overlay of five experiments. The 2-ethoxyethyl acetate rate constant measured is  $10.56 \pm 1.31 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .

**3-Ethoxyacrylic acid ethyl ester OH rate  
constant w/ Trans-2-Butene**

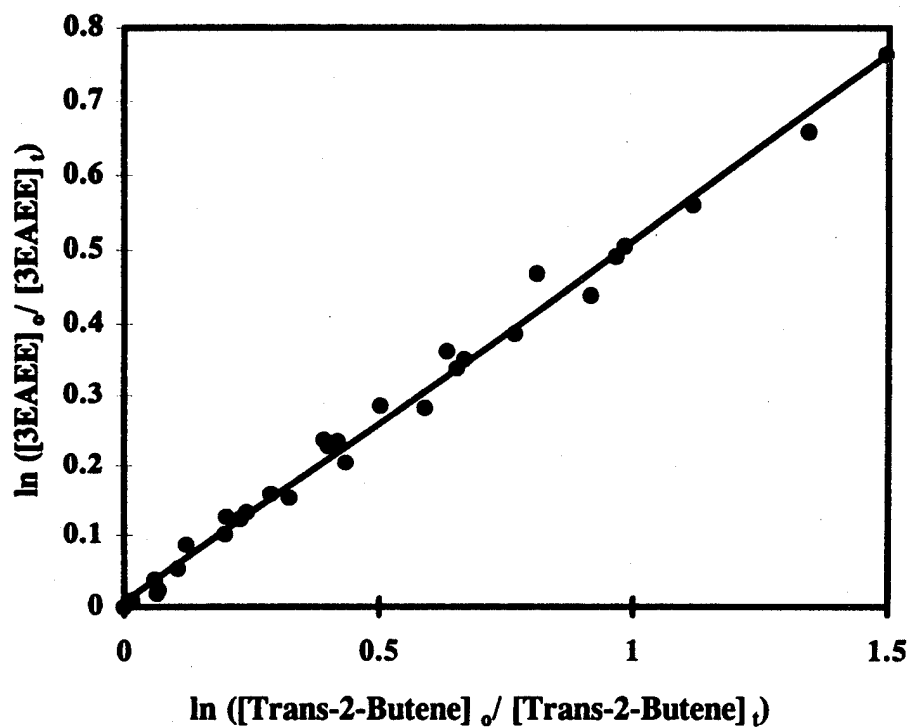


Figure 6. 2-Ethoxyacrylic acid ethyl ester relative plot with trans-2-butene as the reference compound. This is an overlay of five experiments. The 2-ethoxyacrylic acid ethyl ester rate constant measured is  $33.30 \pm 1.22 \times 10^{-12} \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$ .

## Trans-2-Heptene OH rate constant w/ Butene

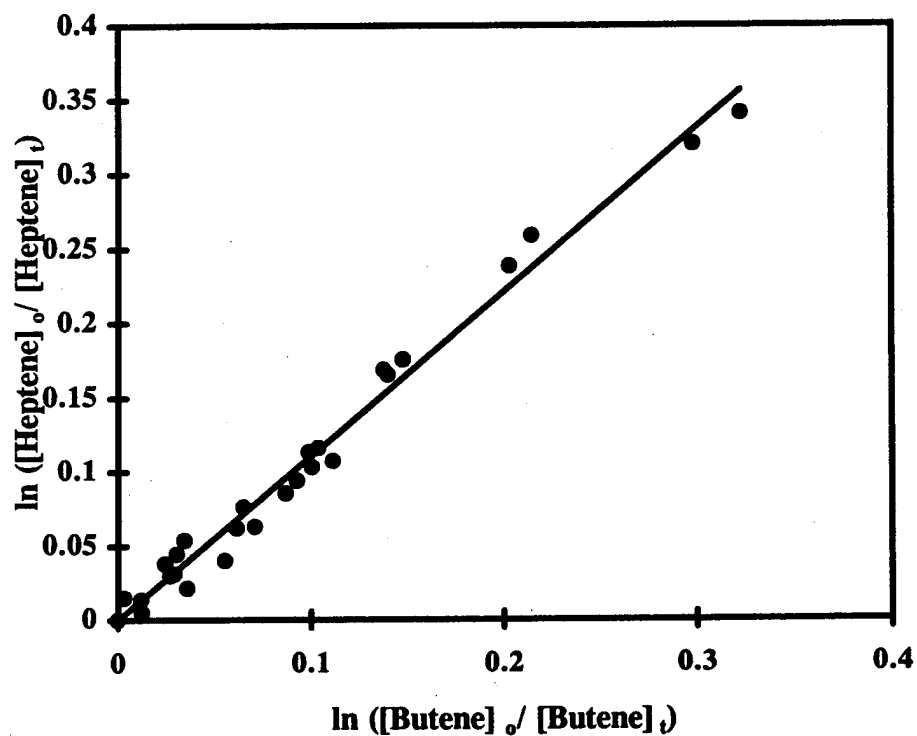


Figure 7. Trans-2-heptene relative plot with butene as the reference compound. This is an overlay of five experiments. The trans-2-heptene rate constant measured is  $6.86 \pm 0.5 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .

4-Methyl-2-Pentanone OH rate constant w/  
Butene

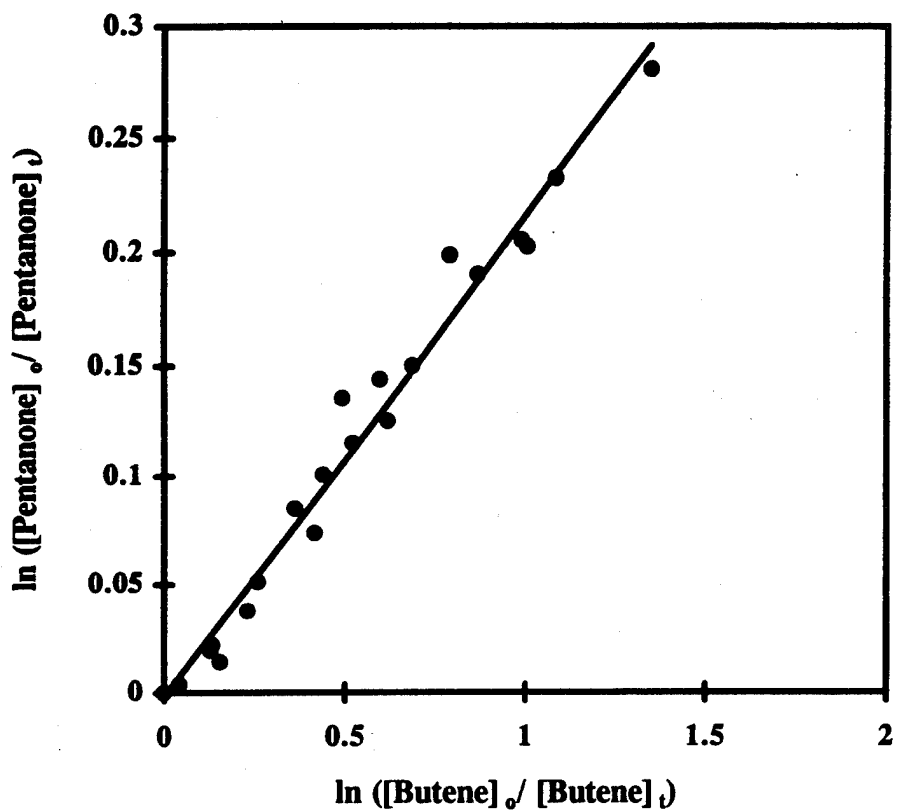


Figure 8. 4-Methyl-2-pentanone relative plot with butene as the reference compound. This is an overlay of five experiments. The 4-methyl-2-pentanone rate constant measured is  $1.40 \pm 0.06 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .

### Trans-4-Octene OH rate constant w/ Butene

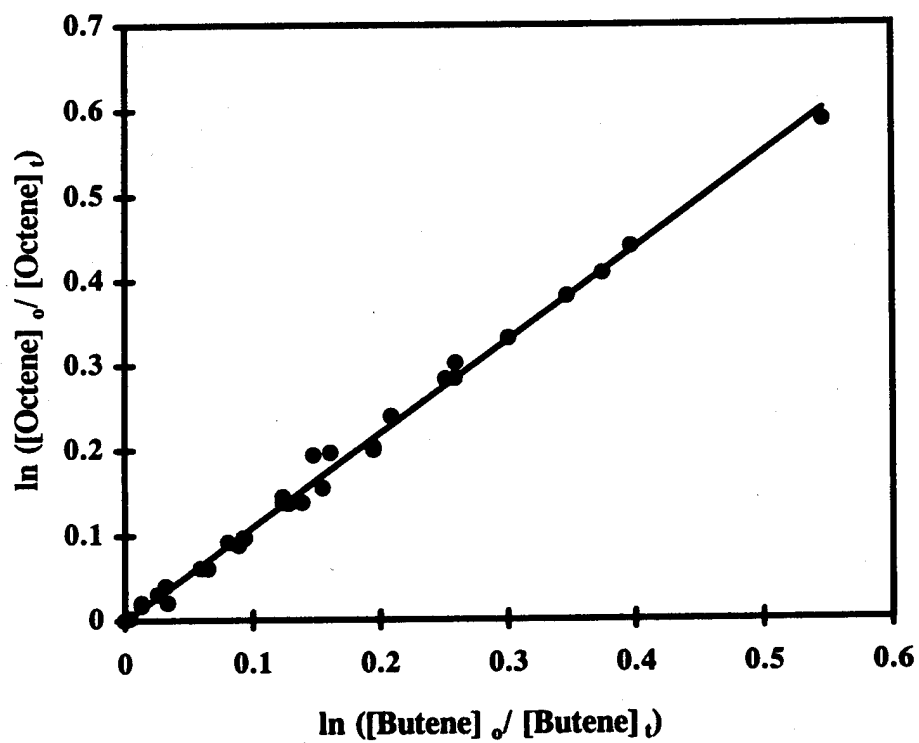


Figure 9. Trans-4-octene relative plot with butene as the reference compound. This is an overlay of five experiments. The trans-4-octene rate constant measured is  $6.93 \pm 0.29 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .

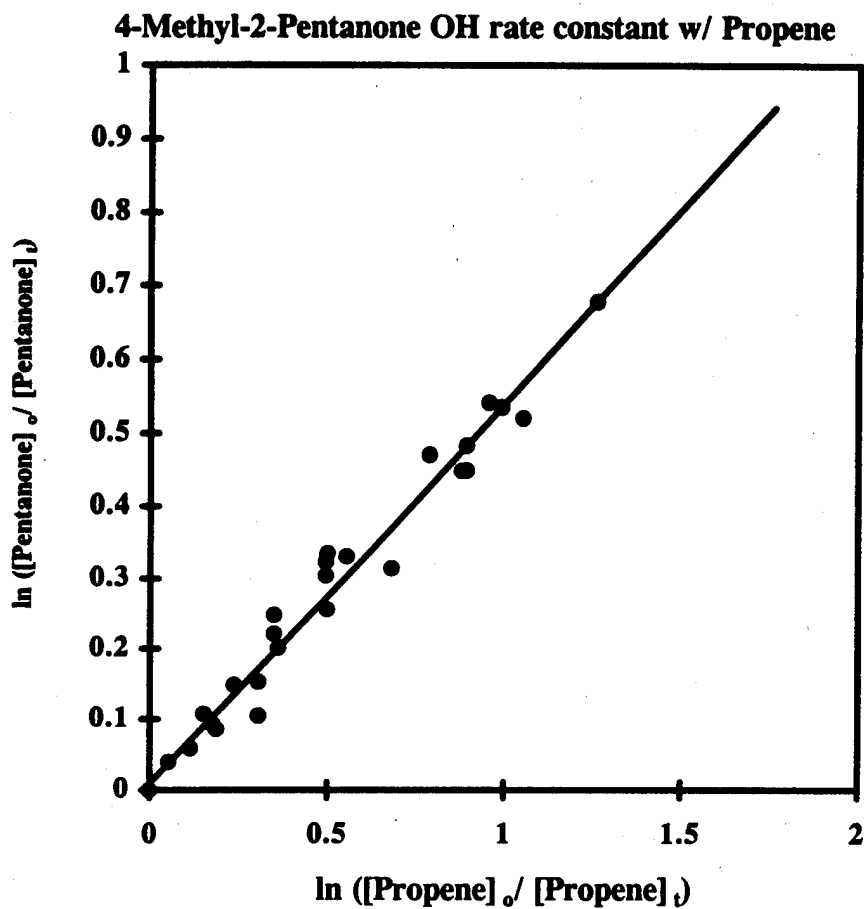


Figure 10. 4-Methyl-2-pentanone relative plot with propene as the reference compound. This is an overlay of five experiments. The 4-methyl-2-pentanone rate constant measured is  $1.40 \pm 0.07 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .

## 2-Ethoxyethanol OH rate constant w/ n-Heptane

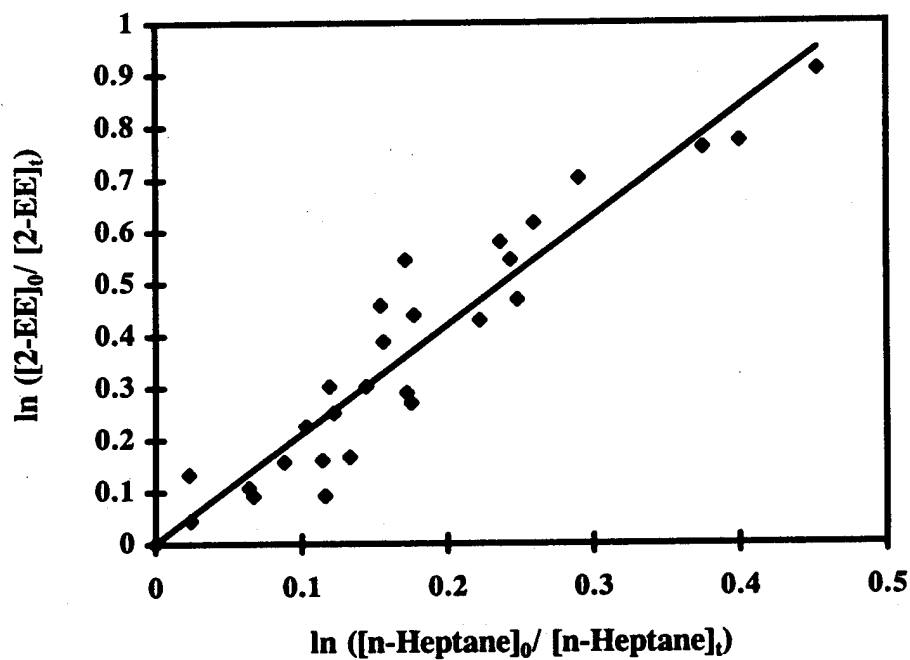


Figure 11. 2-Ethoxyethanol relative plot with n-heptane as the reference compound. This is an overlay of five experiments. The 2-ethoxyethanol rate constant measured is  $1.5 \pm 0.1 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .

Table 1. Compounds studied, Chemical Structure and OH Rate Constants Measured.

Compound	OH Rate constant (units of $10^{-11}$ $\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$ )	Reference compound
4-methyl-2-pentanone	$1.401 \pm 0.072$	propene
$(\text{CH}_3)_2\text{CHCH}_2\text{COCH}_2$	$1.403 \pm 0.064$	trans-2-butene
trans-4-octene	$6.77 \pm 0.5$	propene
$\text{CH}_3(\text{CH}_2)_2\text{CH}=\text{CH}(\text{CH}_2)_2\text{CH}_3$	$6.93 \pm 0.29$	trans-2-butene
trans-2-heptene	$6.70 \pm 0.23$	propene
$\text{CH}_3(\text{CH}_2)_3\text{CH}=\text{CHCH}_3$	$6.86 \pm 0.52$	trans-2-butene
n-butyl acetate	$0.571 \pm 0.094$	propene
$\text{CH}_3\text{CO}_2(\text{CH}_2)_3\text{CH}_3$	$0.555 \pm 0.086$	n-butane
n-propyl acetate	$0.342 \pm 0.087$	propene
$\text{CH}_3\text{CO}_2(\text{CH}_2)_2\text{CH}_3$	$0.356 \pm 0.085$	n-butane
n-pentyl acetate	$0.753 \pm 0.084$	propene
$\text{CH}_3\text{CO}_2(\text{CH}_2)_4\text{CH}_3$	$0.754 \pm 0.056$	n-butane
2-ethoxyethyl acetate	$1.056 \pm 0.131$	propene
$\text{CH}_3\text{CO}_2\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_3$	$1.066 \pm 0.063$	n-butane
2-ethoxyethyl isobutyrate	$1.356 \pm 0.232$	propene
$(\text{CH}_3)_2\text{CHCO}_2\text{CH}_2\text{CH}_2\text{OC}_2\text{H}_5$	$1.365 \pm 0.17$	trans-2-butene
2-ethoxyethyl methacrylate	$2.722 \pm 0.206$	propene
$\text{H}_2\text{C}=\text{C}(\text{CH}_3)\text{CO}_2\text{CH}_2\text{CH}_2\text{OC}_2\text{H}_5$	$2.803 \pm 0.338$	trans-2-butene
4-pentene-1-yl acetate	$4.340 \pm 0.385$	propene
$\text{CH}_3\text{CO}_2(\text{CH}_2)_3\text{CH}=\text{CH}_2$	$4.290 \pm 0.288$	trans-2-butene
3-ethoxyacrylic acid ethyl ester	$3.330 \pm 0.122$	trans-2-butene
$\text{CH}_3\text{CH}_2\text{OCH}=\text{CHC}(\text{O})\text{OCH}_2\text{CH}_3$		

The rate constant obtained here for the OH radical reaction with 4-methyl-2-pentanone is  $1.401 \pm 0.072 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  with propene as a reference and  $1.403 \pm 0.064 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  with trans-2-butene as the reference (Figures 8,10). Both values are in excellent agreement with the literature values and within experimental error of each other [18-21]. The rate constant obtained for trans-4-octene relative to propene is  $6.77 \pm 0.50 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  while its value relative to trans-2-butene is  $6.93 \pm 0.29 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (Figures 4,9). For trans-2-heptene these rate constants are  $6.70 \pm 0.23 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  with propene as a reference and  $6.86 \pm 0.52 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  with trans-2-butene as a reference (Figures 3,7). There are no published literature rate constants for OH degradation for trans-2-heptene and trans-4-octene. Even though the reference OH rate constants differ by a factor of three each of the two measured rate constants for trans-2-heptene, trans-4-octene, and 4-methyl-2-pentanone are within experimental error of one another.

The reaction rate constant of n-butyl acetate with OH radicals was measured to be  $5.71 \pm 0.94$  and  $5.55 \pm 0.86$  ( $\times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ), with propene and n-butane as references respectively. The measured OH reaction rate constants for n-propyl acetate are  $3.42 \pm 0.87 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  with propene as a reference and  $3.56 \pm 0.85 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  with butane as a reference. The rate constants for OH reactions with n-pentyl acetate are  $7.53 \pm 0.84$  and  $7.54 \pm 0.56 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  with propene and n-butane as references, respectively. For OH radical reaction with n-pentyl acetate, no previous relative or absolute reaction rate constants have been reported in the literature.

The only literature value for the reaction of OH radicals with 2-ethoxyethyl acetate is  $13 \pm 2 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  based on an absolute technique [18]. Our values are  $10.56 \pm 1.31$

and  $10.66 \pm 0.63 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  with propene and n-butane references, respectively. These values are within experimental error of each other.

No previous relative rate constants for the reactions of 2-ethoxyethyl isobutyrate, ethoxyethyl methacrylate, and 4-pentene-1-yl acetate with OH radicals have been reported in the literature. The rate constants measured for this report are  $13.56 \pm 2.32$ ,  $27.22 \pm 2.06$ , and  $43.40 \pm 3.85 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  for 2-ethoxyethyl isobutyrate, 2-ethoxyethyl methacrylate, and 4-pentene-1-yl acetate, respectively. These rate constants were measured using propene as a reference compound. The measured OH reaction rate constants for 2-ethoxyethyl isobutyrate, 2-ethoxyethyl methacrylate, and 4-pentene-1-yl acetate with trans-2-butene as a reference compound are  $13.65 \pm 1.7$ ,  $28.03 \pm 3.38$ , and  $42.90 \pm 2.88 (x 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1})$ , respectively. These values are in excellent agreement with the rate constants measured with propene as the reference compound. The rate constant for OH degradation of 3-ethoxyacrylic acid ethyl ester was based solely on trans-2-butene, and this value is  $33.30 \pm 1.22 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (Figure 6).

The OH rate constant for 2-ethoxyethanol has been reported twice previously in the literature [22,23]. The average value of the reported literature OH + 2-ethoxyethanol rate constant is approximately  $1.85 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . An OH rate constant of  $1.5 \pm 0.1 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (Figure 11) is reported here.

## B. PRODUCT STUDIES OF 2-ETHOXYETHYL ACETATE

The products of the reaction of 2-ethoxyethyl acetate (2EEA) with OH were characterized and quantified. A possible reaction mechanism was determined from the product identification. The OH abstracts hydrogen predominantly from the ethoxy end of the molecule. The main products are 1,2 ethanediol acetate formate (EAF), ethylene glycol diacetate (EGD), and ethyl

formate. EAF was synthesized by Radian Corporation; EGD and ethyl formate was purchased from Aldrich chemical company. Product identification was confirmed from comparison of experimental data with the pure compound retention time, mass spectrum and infrared spectrum. Figures 12-22 highlight these results. Carbon monoxide (CO) was observed in the large chamber using the long-path FTIR.

To quantify product formation from OH + 2EEA, a series of experiments monitoring product growth and 2EEA loss was carried out. Figures 23-25 display the type of data generated. These data highlight the loss of 2EEA and the rise of the three products. The molar yield can be determined from the slope of the least squares fit of a plot of product concentration versus reactant concentration. EAF accounts for 32.9 mole % of the 2EEA lost due to reaction; EGD accounts for 3.1 mole % of the lost carbon; and ethyl formate accounts for 49.2 mole % of the reacted 2EEA. Therefore about 85 mole % of the 2EEA lost in the reaction with OH can be attributed to the products observed.

The 2,4-dinitrophenylhydrazine (DNPH) study of the products of the hydroxyl radical reaction with 2EEA was performed as described in the Experimental Section. The main observation was the growth of an analyte peak at retention time 8.520 minutes. This is most likely acetaldehyde. This retention time compares well to retention time standards for this compound and is a reasonable product in the reaction mechanism for 2EEA. If there is cleavage of the O-C bond at either of the methylene groups bonded to the ether oxygen of the ethoxy group, the resulting  $\cdot\text{CH}_2\text{-CH}_3$  or  $\text{O-CH}_2\text{-}\cdot\text{CH}_3$  radical could subsequently result in the formation of acetaldehyde. However, as a result of instrumental problems, no quantitation of this product was possible by the close of this contract.

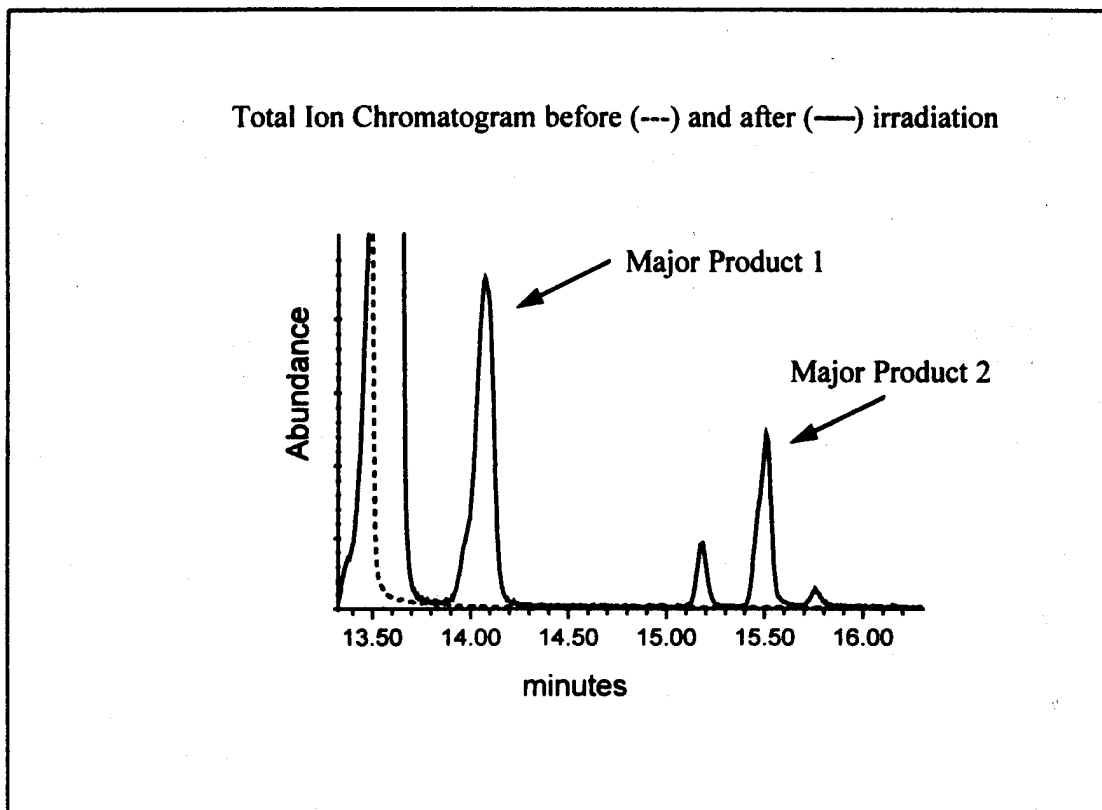


Figure 12. Total Ion Chromatogram (TIC) from GC/MS of 2-ethoxyethyl acetate before (dashed line) and after (solid line) OH generation.

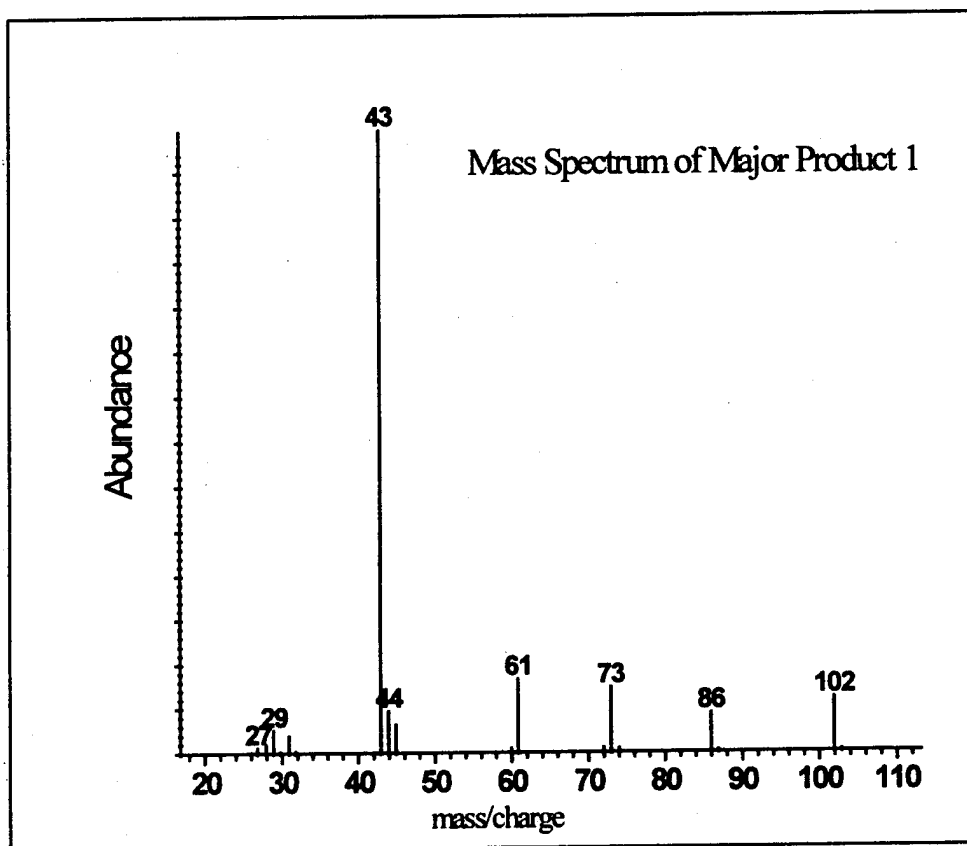


Figure 13. Mass spectrum of Major Product 1 shown in Figure 12.

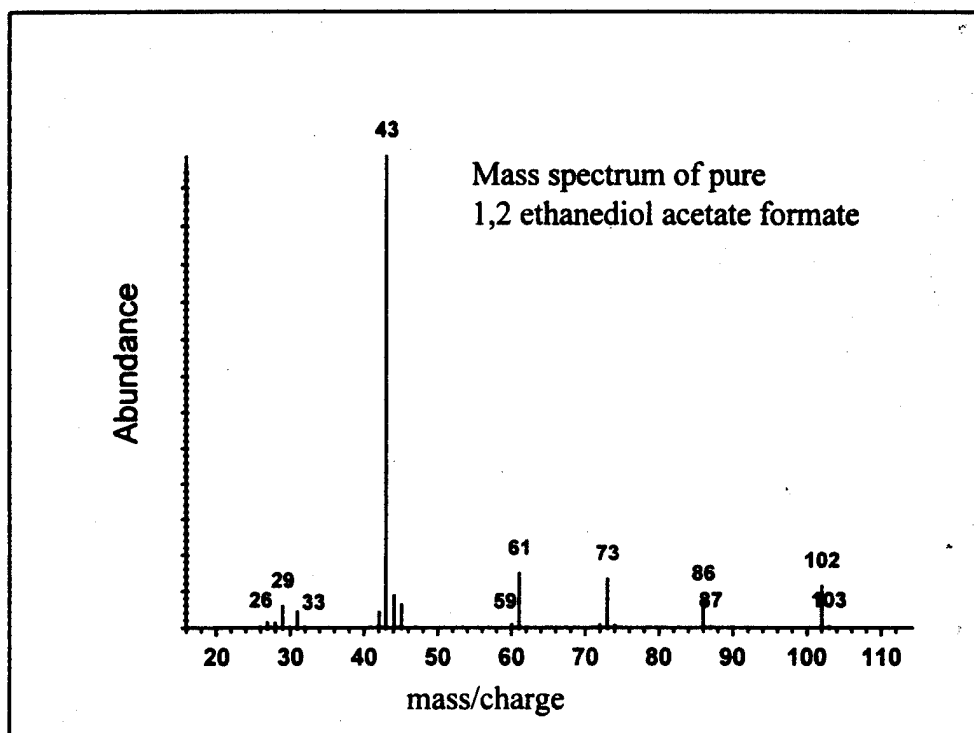


Figure 14. Mass spectrum of pure 1,2 ethanediol acetate formate (EAF).

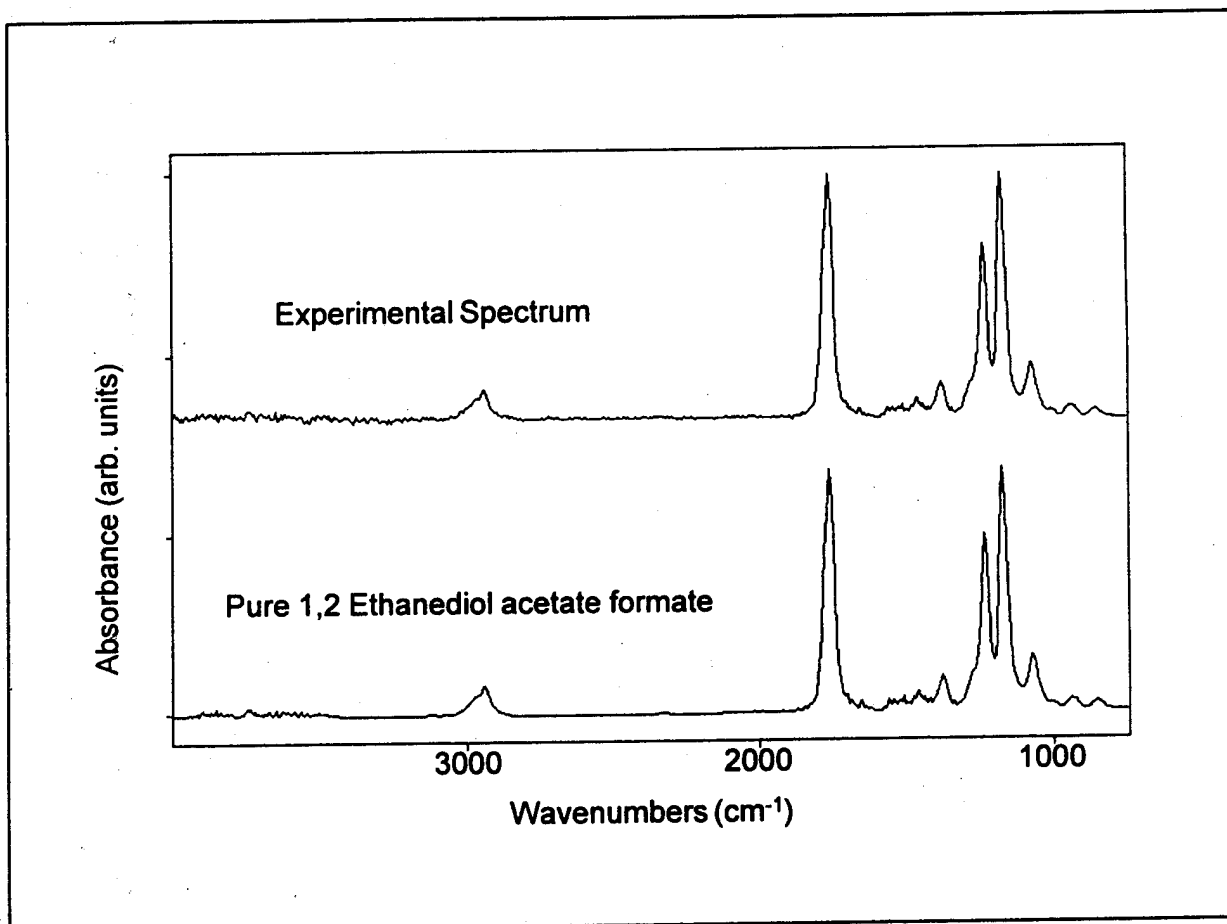


Figure 15. Comparison of data from GC/IRD of Major Product 1 and pure EAF.

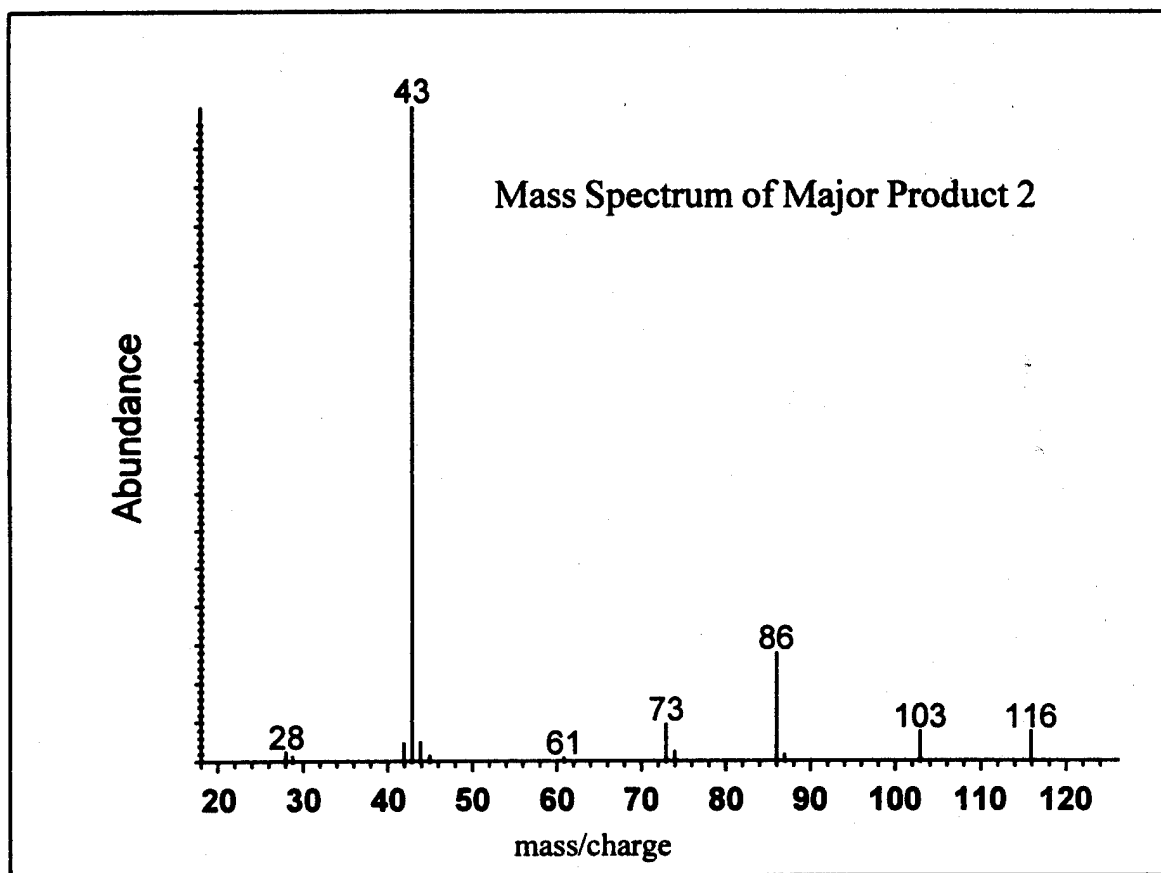


Figure 16. Mass spectrum of Major Product 2 shown in Figure 12.

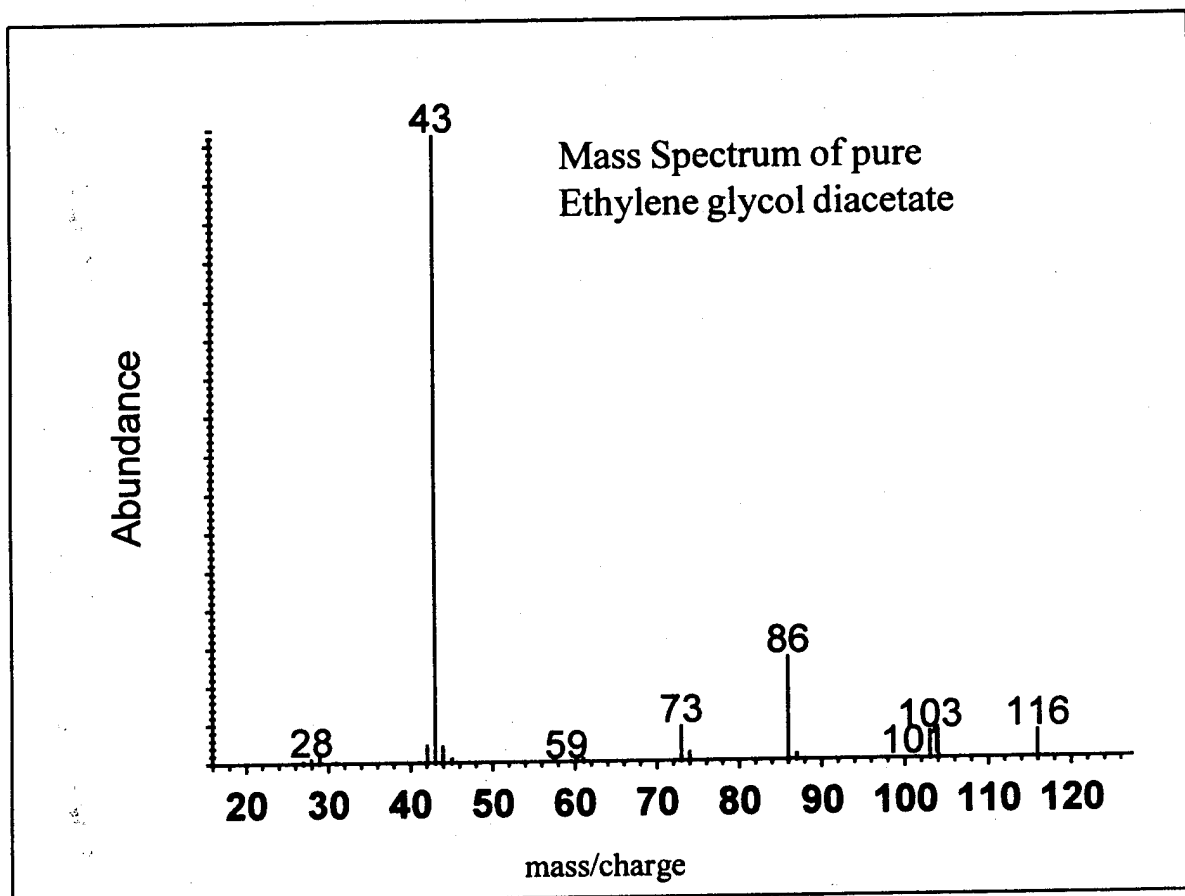


Figure 17. Mass spectrum of pure ethylene glycol diacetate (EGD).

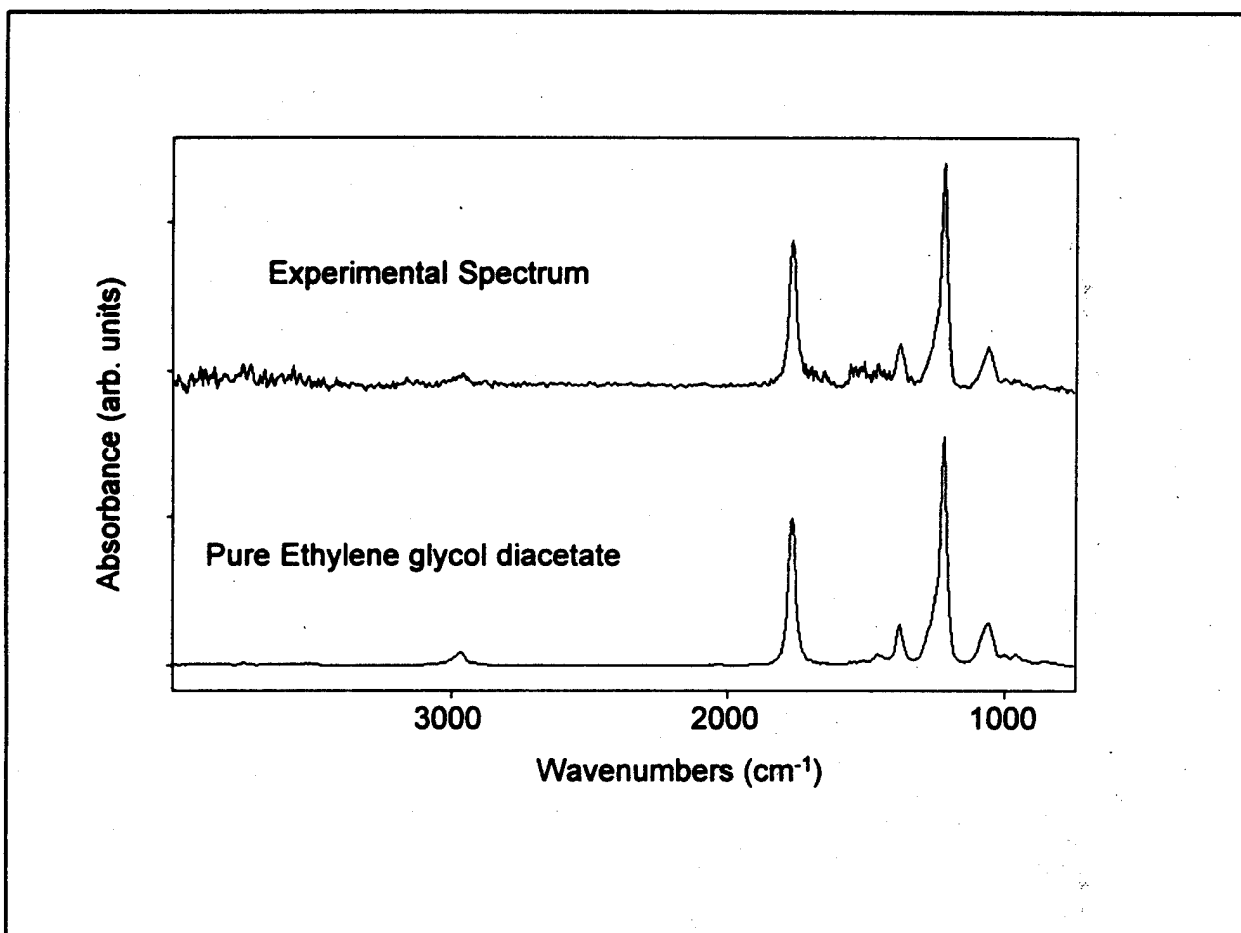


Figure 18. Comparison of data from GC/IRD of Major Product 2 and pure EGD.

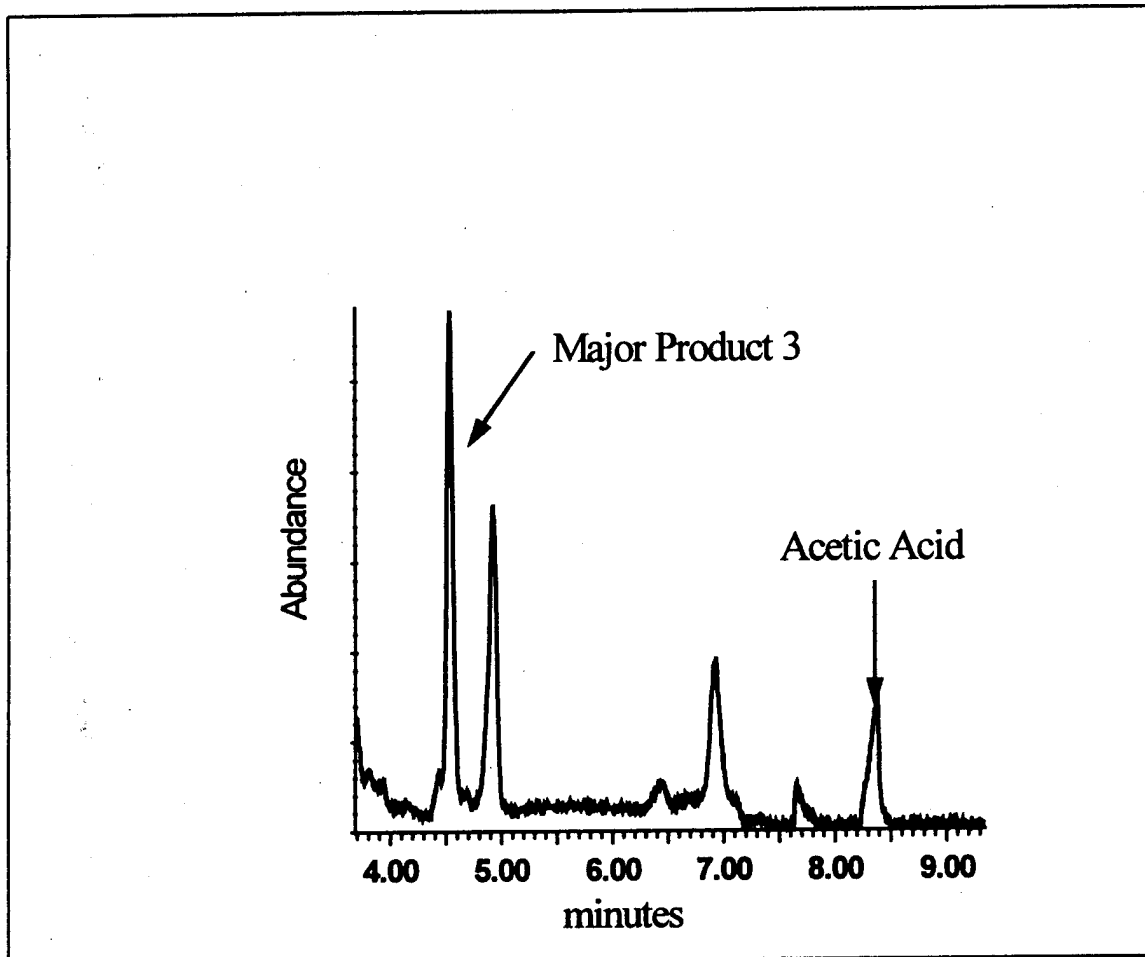


Figure 19. TICs from GC/MS of 2EEA after OH generation.

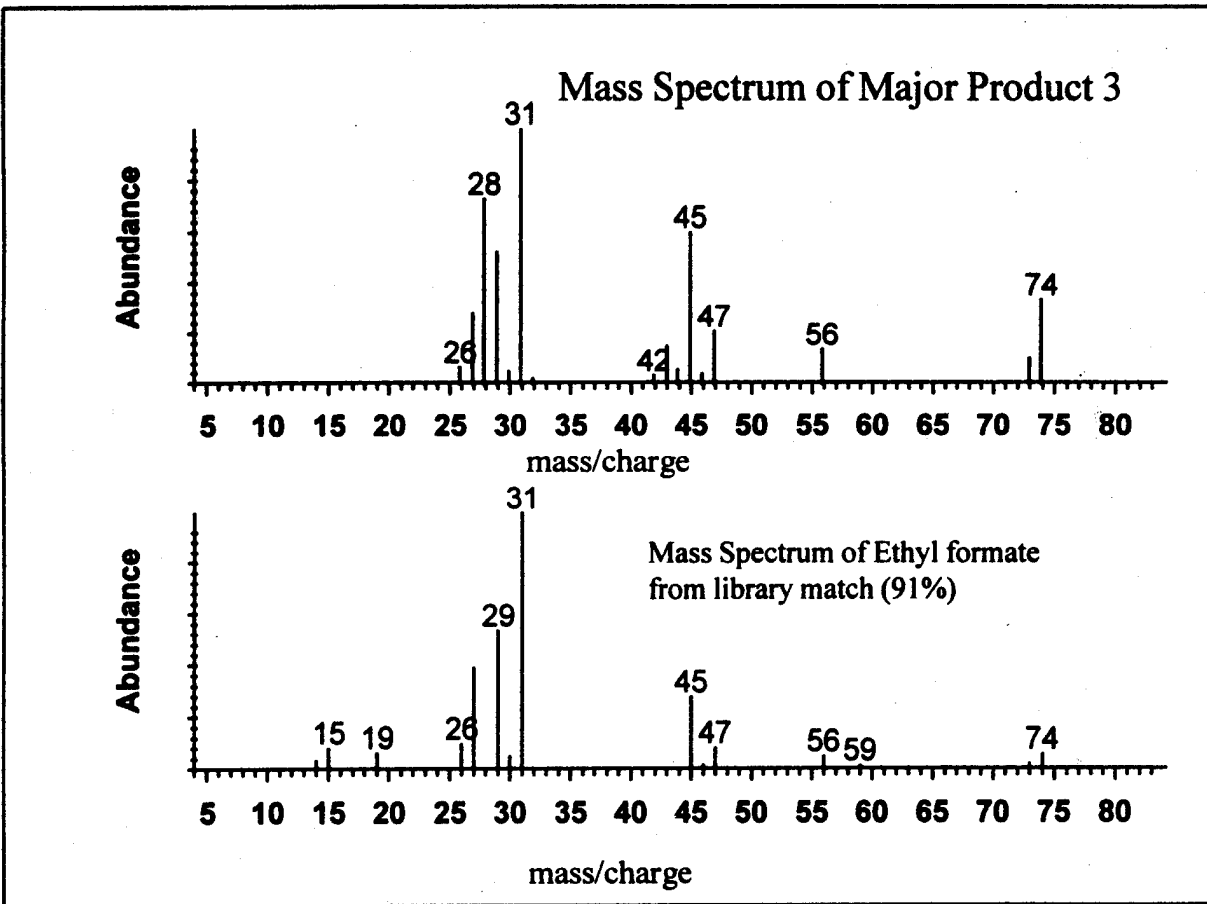


Figure 20. Mass spectrum of Major Product 3 and library match comparison.

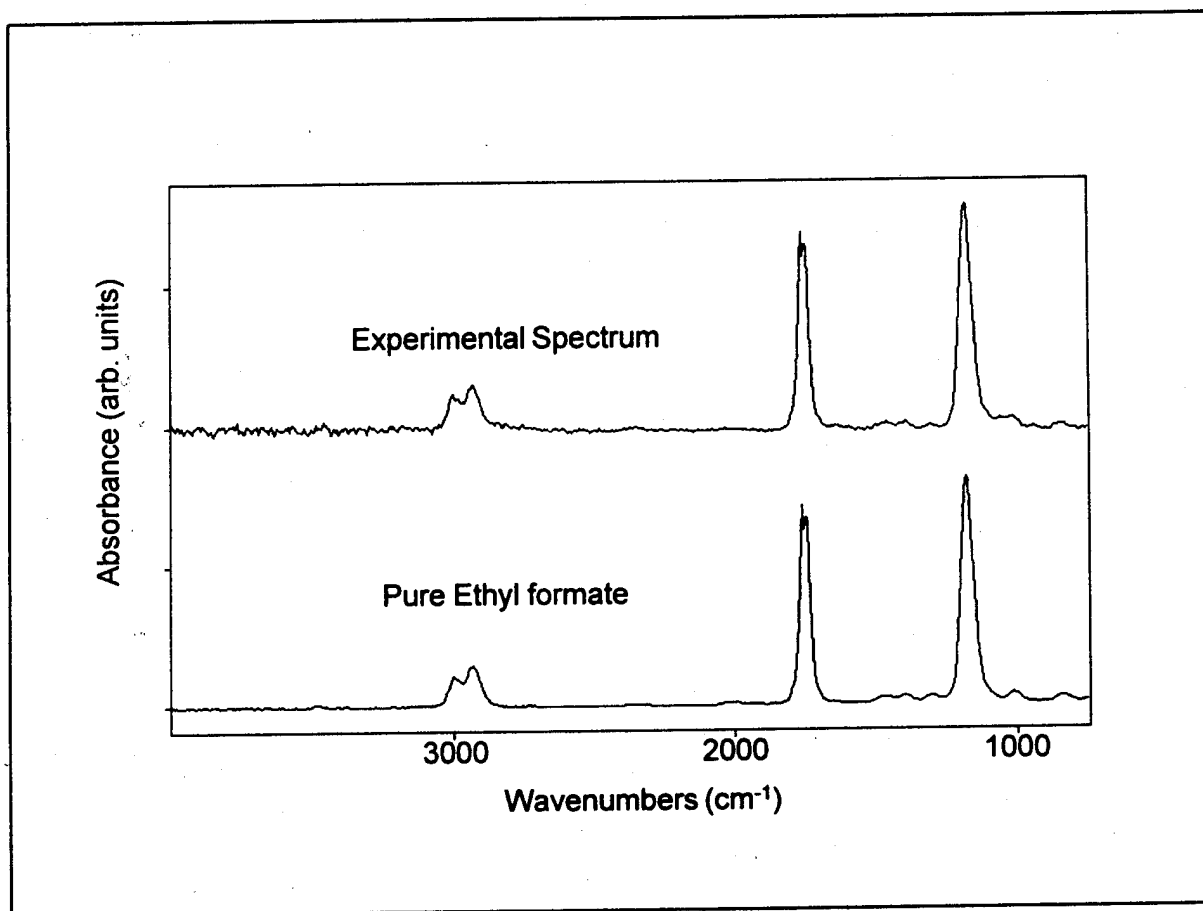


Figure 21. Infrared spectrum of Major Product 3. Infrared library matched this spectrum to formic acid, *methyl* ester. The library did not have formic acid, *ethyl* ester.

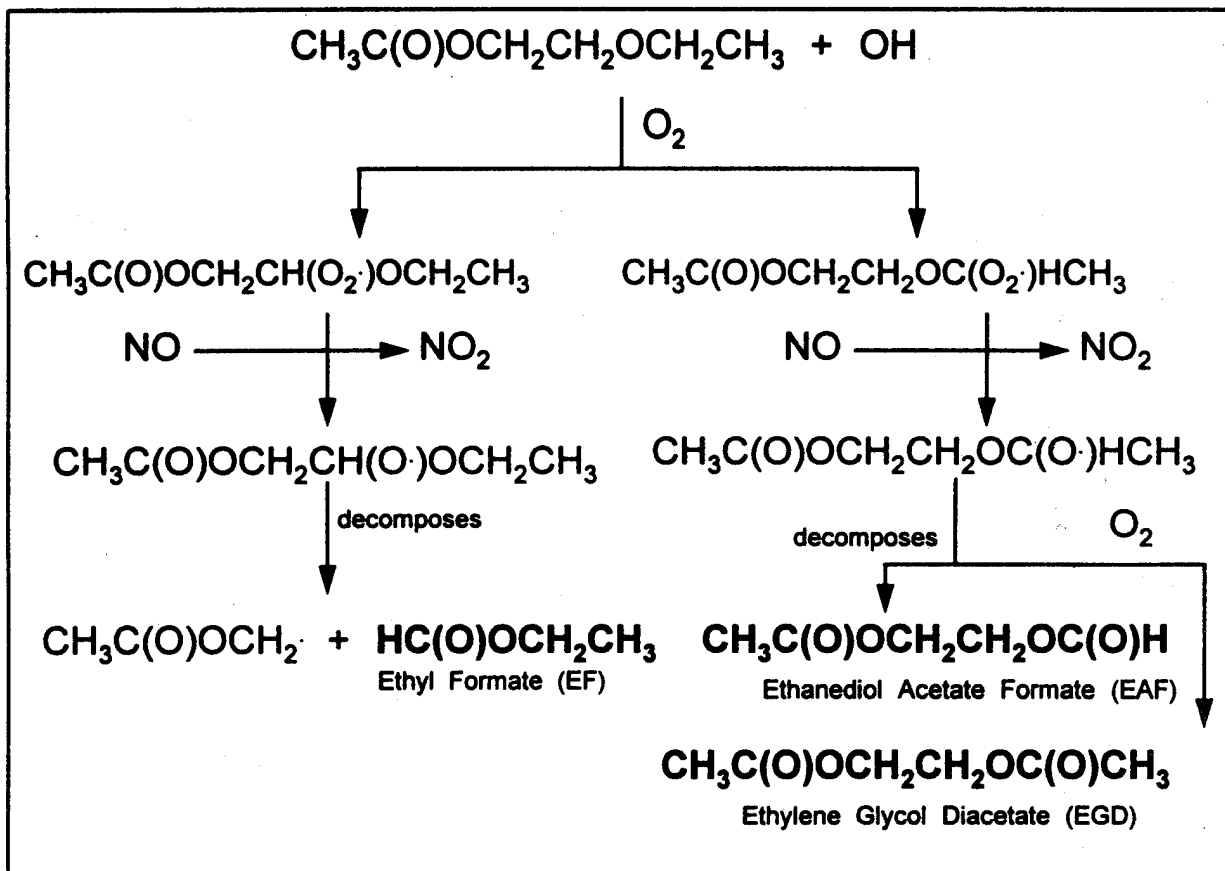


Figure 22. Proposed reaction mechanism for the production of EAF, EGD and EF after OH hydrogen abstraction from 2-ethoxyethyl acetate.

### EAF FORMED vs. 2EEA LOST

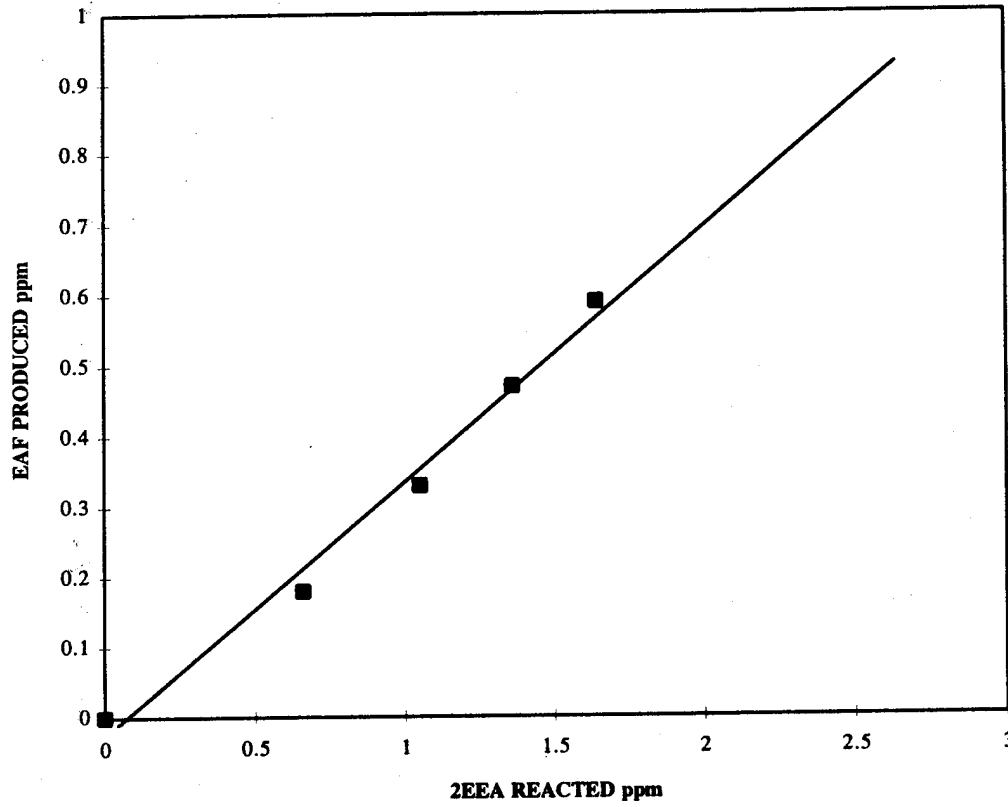


Figure 23. EAF production versus 2-ethoxyethyl acetate loss.

### EGD FORMED VS. 2EEA LOST

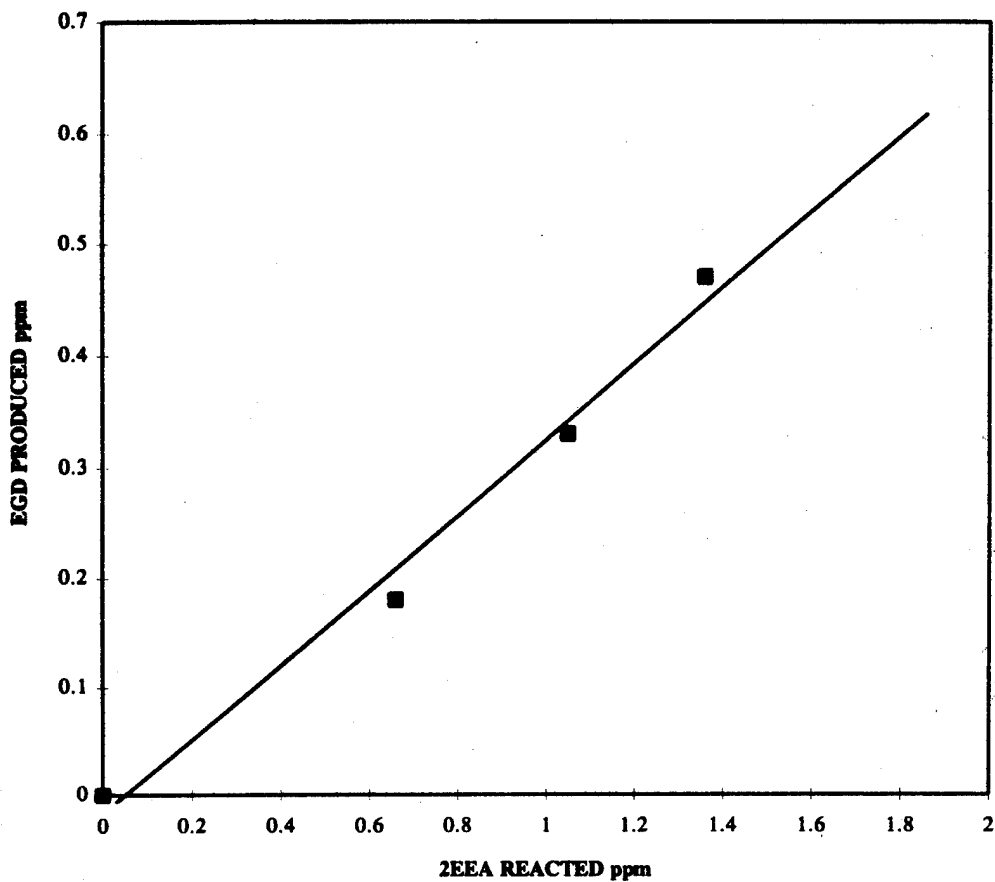


Figure 24. EGD production versus 2-ethoxyethyl acetate loss.

### ETHYL FORMATE FORMED VS. 2EEA LOST

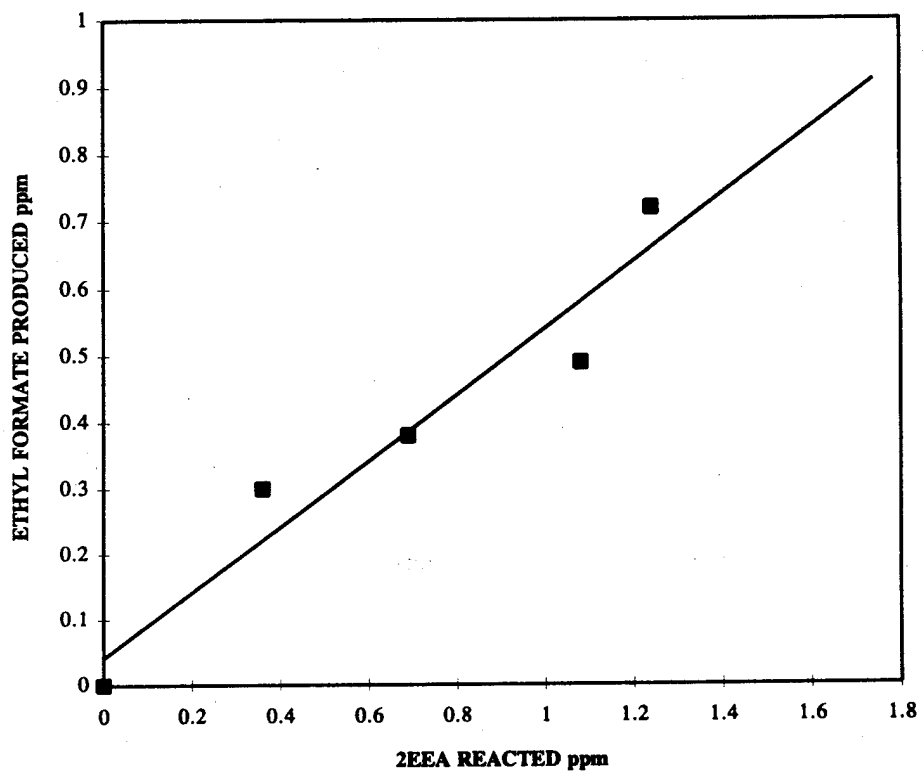


Figure 25. Ethyl formate production versus 2-ethoxyethyl acetate loss.

## SECTION IV

### OBSERVATIONS

#### A. OH RATE CONSTANTS OF SOLVENTS STUDIED

It is generally accepted that the reaction of OH radicals with hydrocarbons proceeds via hydrogen abstraction from the C-H bonds for alkanes and, for alkenes, by OH addition to the carbon-carbon double bond [24,25]. The similar OH reaction rate constants of  $6.85$  and  $6.78 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  for trans-4-octene and trans-2-heptene, respectively, strongly suggest that the OH radical interacts with the two alkenes similarly. The atmospheric lifetime of 4-methyl-2-pentanone is 20 h; of trans-4-octene is 4h; and trans-2-heptene is 4h. This lifetime is calculated using an average OH concentration of  $1 \times 10^6 \text{ molecules cm}^{-3}$  [26].

The few literature reports on the kinetics and reaction mechanisms of simple esters seem to agree that the OH radical reacts predominantly with the alkoxy end on the esters rather than the acyl end and that there is a general increase in the rate constants with increasing substitution on the alkoxy end of the ester [27-30]. Figure 26 shows a plot of the number of methylene groups ( $\text{CH}_2$ ) of the simple ester homologous series methyl acetate through pentyl acetate versus the corresponding relative rate constant obtained in this study. A linear correlation is observed in this figure between the number of  $\text{CH}_2$  groups and the OH reaction rate constant. This linear relationship further supports the argument that hydrogen abstraction occurs at the alkoxy end of these compounds. Experiments to determine the products formed in the OH reactions with these acetates can elucidate this hypothesis. As the alkoxy chain adds more methylene groups the steric and electronic effects of the  $-\text{C}(\text{O})\text{O}-$  group will be lessened.

The OH rate constants for n-propyl acetate reported here ( $3.42 \pm 0.87$  and  $3.56 \pm 0.85 \times$

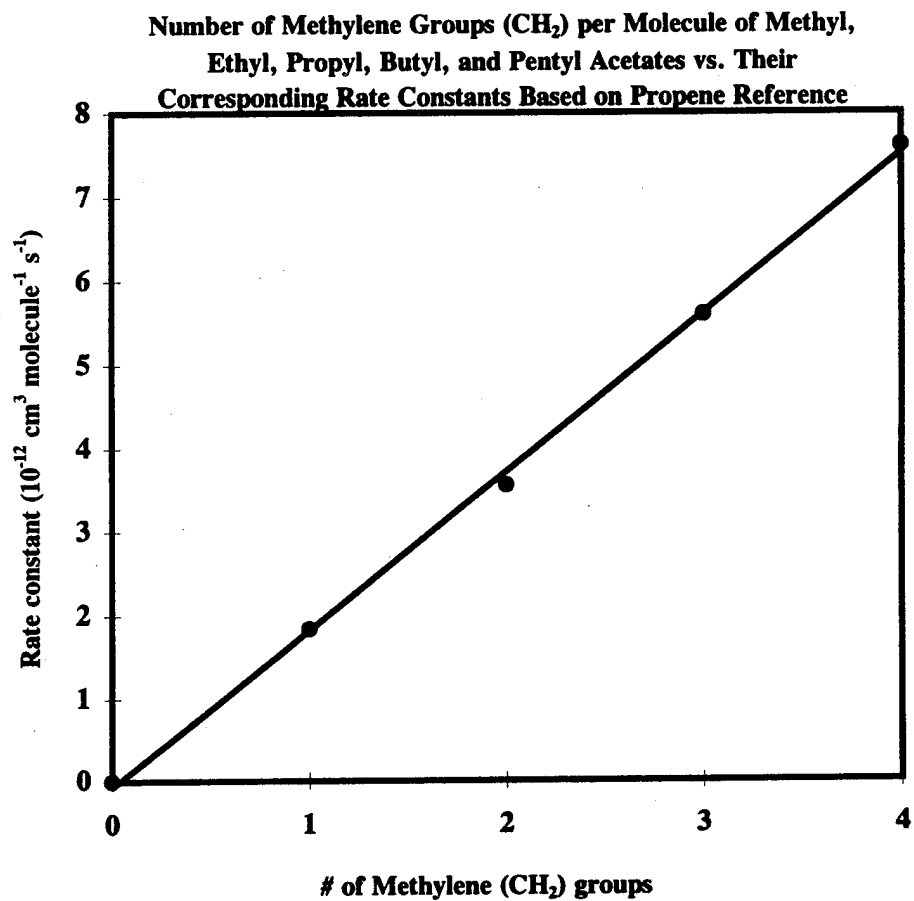


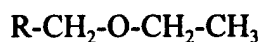
Figure 26. Plot of number of methylene groups versus OH reaction rate constant for methyl, propyl, butyl, and pentyl acetates.

$\times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ) are in excellent agreement with the values reported by Wallington ( $3.45 \pm 0.34 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ) and Winer ( $3.4 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ) [28,30]. The literature rate constant for OH + n-butyl acetate ( $4.3 \pm 0.8$  and  $4.15 \pm 0.30 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , references 23 and 30, respectively) is slightly lower than the measured value in this report (average  $5.6 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ) [23]. No previous literature reports on the OH reaction rate constant with n-pentyl acetate are available.

The rate constants obtained for n-propyl acetate, n-butyl acetate, pentyl acetate, and 2-ethoxyethyl acetate indicate that they will be somewhat reactive in the troposphere, with estimated lifetimes of 81 h, 49 h, 37 h, 26 h, respectively (based on  $1 \times 10^6 \text{ OH radicals cm}^{-3}$ ). The atmospheric lifetimes for 2-ethoxyethyl isobutyrate, 2-ethoxyethyl methacrylate, 4-penten-1-yl acetate, and 3-ethoxyacrylic acid ester are 20 h, 10 h, 6 h, and 8 h, respectively, based on their measured OH reaction rate constants. The 2-ethoxyethanol lifetime of 19 h is calculated based on its measured OH reaction rate constant.

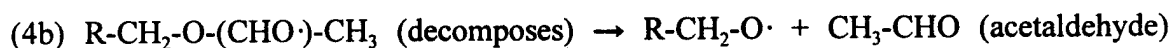
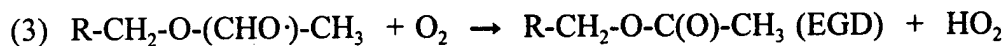
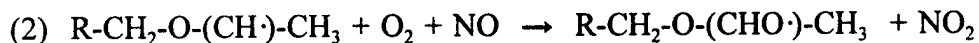
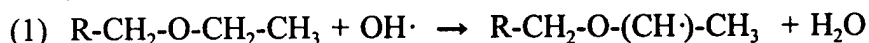
## B. PRODUCTS OF 2-ETHOXYETHYL ACETATE

The reaction mechanism proposed in Figure 22 is supported by the product identification data. Because 2-ethoxyethyl acetate is a large molecule, there is the expectation that the OH radical would abstract hydrogen from one of five possible carbons. However, the products of the reaction of OH with 2-ethoxyethyl acetate suggest strongly that the OH abstracts hydrogen principally from either of the two methylene groups bonded to the ether oxygen of the ethoxy functional group;



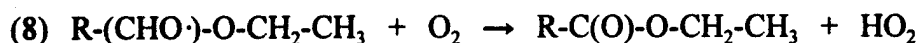
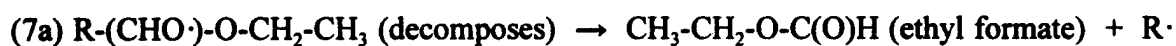
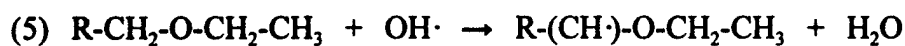
where the R-group is  $\text{CH}_3\text{-C(O)-O-CH}_2\text{-}$ .

The experimental parameters were set to minimize other side reactions and highlight the first OH abstraction step. Both the products EAF and EGD are structurally similar to 2-ethoxyethyl acetate (Figure 22) and result from the same initial H abstraction at the right methylene group. Depending on the disposition of the alkoxy radical formed in Reaction (2);



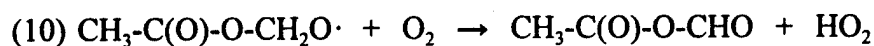
it can form EGD (Reaction (3)) through further reaction with  $\text{O}_2$  or it can decompose through one of two pathways to form EAF (Reaction (4a)) or acetaldehyde (Reaction (4b)) plus another alkoxy radical,  $\text{R-CH}_2\text{-O}\cdot$ . No product was observed as a result of the subsequent oxidation of this radical to the corresponding aldehyde,  $\text{R-CHO}$ . Further decomposition could follow a similar reaction sequence as shown in Reactions (10) and (11) eventually resulting in the same products as for the  $\text{R}\cdot$  radical from Reaction (7a).

The other major product observed is ethyl formate and is formed from abstraction from the inner or left methylene group depending on the disposition of the alkoxy radical formed in Reaction (6).



If the radical decomposes according to Reaction (7a), the result is ethyl formate. If it decomposes by Reaction (7b), the result is an unobserved product, R-CHO, plus an alkoxy radical whose likely disposition is the formation of acetaldehyde. The diester product formed in Reaction (8) was not observed and it is assumed the primary pathway was through decomposition as in Reactions (7a) and (7b).

If the disposition of the R· radical formed in Reaction (7a) followed according to;



this would result in the formation of the product formic acetic anhydride (Reaction (10)). In the presence of water, this would decompose to acetic acid and formic acid, both of which were consistently observed in the GC measurements. The alkoxy radical formed in Reaction (9) could also decompose, possibly resulting in the products carbon monoxide, carbon dioxide, formaldehyde and acetyl radicals. Carbon monoxide was observed in the large-chamber reaction system by FTIR. In an urban oxidation system, the acetyl radicals could result in the formation

of peroxyacetyl nitrate (PAN).

The formation rate of EAF to EGD is about 10:1 indicating the primary pathway for disposition of the alkoxy radical formed in Reaction (5) is through decomposition. Ethyl formate is also formed through decomposition of the alkoxy radical from Reaction (6). Further, the formation of acetaldehyde from other decomposition pathways indicates the primary disposition mode of the alkoxy radical adjacent to the ether linkage is through decomposition. This is in agreement with previously published report [31] on the branched ether, ethyl *t*-butyl ether. In this case, the primary point of attack by OH is on the methylene group of the ethyl side of the ether similar to 2EEA. The primary product, *t*-butyl formate, formed as result of decomposition of the alkoxy radical. The minor product, *t*-butyl acetate, is formed in a ratio of about 1:5 with the *t*-butyl formate.

The structure of the measured products EGD, EAF and ethyl formate, are such that they could not have come from the same molecule thus resulting the reasonably good observation of products from almost 85% of the 2EEA reacted. However, the total carbon recovered is only about 55% with the primary error occurring from the balance of products not observed following the formation of ethyl formate. Because of problems with the HPLC, we were unable to quantitate the yields for acetaldehyde and formaldehyde which likely account for a substantial portion of the unrecovered carbon. Acetic acid, formic acid and carbon monoxide were observed qualitatively but were not quantitated and may also represent a significant portion of the product yield.

## SECTION V

### CONCLUSIONS/RECOMMENDATIONS

The list of compounds studied under this contract consists of alkenes, acetates, carbonyls and ethers. This research has shown them to be reactive with the key radical in the atmosphere, the OH radical, and to have lifetimes of less than a day. They are not appreciably photolyzed by sunlight, so that their primary mode of atmospheric removal is through reaction with OH. The alkenes in this study have a fast OH rate constant indicating a short atmospheric lifetime. The acetates have a much longer atmospheric lifetime due to a slower OH rate constant. This longer atmospheric lifetime suggests the acetate compound may build up in the atmosphere. Addition of an acetate group to a hydrocarbon chain slows the OH reaction rate appreciably compared to a similar alkene compound. The combination of an acetate group and a double bond yields an OH reaction rate similar to the alkenes studied. Addition of an ether oxygen enhances the OH reaction rate as well. However, the OH rate constant is only one side of the atmospheric impact of these solvents.

The reaction products of these compounds may have a profound impact on the chemistry of the atmosphere. The reaction products of VOCs have not been fully explored by the atmospheric research community. This research effort laid the ground work for studying the OH + VOC reaction products. The reaction products of OH with 2-ethoxyethyl acetate are ethyl formate, 1,2-ethanediol acetate formate (EAF), and ethylene glycol diacetate (EGD) (Figure 22). The toxicities of EAF and EGD are unknown at this time, but should be investigated. Ethyl formate is a flammable irritant. The OH rate constant of these products appears to be slow,

indicating a long atmospheric lifetime for these products. It is expected that the other acetates will yield similar types of reaction products as 2-ethoxyethyl acetate. The methyl group ( $\text{CH}_3$ ) of the acetate ( $\text{CH}_3\text{C}(\text{O})\text{O}^-$ ) is not attacked rapidly by the OH radical. Therefore the OH radical abstracts a hydrogen from the carbon chain attached to the acetate group. The radical site on the carbon chain is the site of further chemistry and possibly the site of fragmentation of the molecule (Figure 22). Identifying the products from these slowly reacting acetates is important for assessing their environmental impact. The OH radical adds to the double bond of an alkene yielding an alcohol with a neighboring radical carbon site. The products from the alkene/OH reactions are expected to be alcohols of some type. These alcohols can further react with nitric oxide (NO), nitrogen dioxide ( $\text{NO}_2$ ), or the OH radical to produce organic nitrates and smaller aldehydes and ketones. These nitrates are potentially carcinogens and are implicated as  $\text{NO}_x$  sources and thus sources of tropospheric ozone ( $\text{O}_3$ ).

The atmospheric chemistry of VOCs needs to be understood to assess the atmospheric impact of VOC releases into the troposphere. Determining the OH rate constant of these VOCs is a valuable tool to calculating their atmospheric lifetime. The reaction products for these compounds have not been fully explored under this program and the detailed atmospheric reaction mechanisms remain incomplete. However, the product determination experiments of 2-ethoxyethyl acetate highlight the fact that the reaction mechanisms of these VOCs are likely to be complicated. Understanding a compound's reaction mechanism gives insights into the possible reaction mechanisms of a similar compound. Understanding the atmospheric reaction mechanisms of these compounds, however, is vital to developing new environmentally harmless solvents or to demonstrate that the chemicals now in use do not significantly harm the environment.

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