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Crystal D. Forester  
*West Virginia University*

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**Gas-Phase Reactions of Methamphetamine with Hydroxyl  
Radicals and Ozone**

**Crystal D. Forester**

**Master's Thesis**

**Submitted to the College of Arts and Sciences**

**In partial fulfillment of the requirements for the degree of  
Master of Science in Chemistry**

**Committee Members:**

**Dr. Suzanne Bell, Chair**

**Dr. Harry Finklea**

**Dr. Jonathan Boyd**

**Department of Chemistry**

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**Keywords: Methamphetamine, Hydroxyl Radical, Gas-phase  
reactions**

## ABSTRACT

### Gas-Phase Reactions of Methamphetamine with Hydroxyl Radicals and Ozone

Crystal D. Forester

Gas-phase reactions involving methamphetamine, the hydroxyl radical ( $\text{OH}\cdot$ ), and ozone ( $\text{O}_3$ ) at  $(297 \pm 3)$  K and 1 atmosphere total pressure were investigated. A bimolecular rate constant,  $k_{\text{OH}\cdot+\text{methamphetamine}}$ ,  $(960 \pm 100) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , was measured using the relative rate technique for reactions of methamphetamine with  $\text{OH}\cdot$ . Pseudo first-order techniques were used to measure the bimolecular rate constant,  $k_{\text{O}_3+\text{methamphetamine}}$ ,  $(2.7 \pm 0.5) \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  for reactions of methamphetamine with  $\text{O}_3$ . Product studies to determine the degradation of methamphetamine in the gas-phase were conducted and the products of these reactions were identified. The positively identified methamphetamine/ $\text{OH}\cdot$  and methamphetamine/ $\text{O}_3$  reaction products were: benzaldehyde, ethanedial (glyoxal), and 2-oxopropanal (methylglyoxal). The use of derivatizing agent O-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine (PFBHA) was used to propose phenyl-2-propanone as the other major methamphetamine/ $\text{OH}\cdot$  and methamphetamine/ $\text{O}_3$  reaction product. The elucidation of this other reaction product was facilitated by mass spectrometry of the derivatized reaction products coupled with plausible methamphetamine/ $\text{OH}\cdot$  and methamphetamine/ $\text{O}_3$  reaction mechanisms based on previously published volatile organic compound/ $\text{OH}\cdot$  and volatile organic compound/ $\text{O}_3$  gas-phase reaction mechanisms.

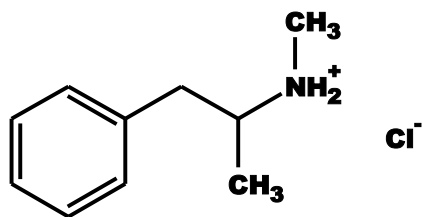
## Background

Clandestine methamphetamine laboratories have been discovered in every state, including the District of Columbia, in the United States (DEA, 2011; ONDCP, 2010). Surveys of law enforcement agencies in 2005 site methamphetamine as a significant problem among the populations that they serve (Nicosia, et al., 2009). Various synthesis methods are used including red phosphorous cook, Birch “Nazi” method and Leuckart method; however, all require the use of hazardous chemicals and precursors. Synthesis often involves pseudoephedrine as a precursor which can be extracted from common over-the-counter cold medications. The free-base form of methamphetamine is initially produced and is subsequently converted into methamphetamine hydrochloride. After conversion to its hydrochloride salt, methamphetamine can be found in pill, powder and crystalline forms and may be ingested orally, snorted, smoked and injected. During the “salting out” phase of synthesis, methamphetamine can deposit on surfaces at concentrations up to 1,000  $\mu\text{g}$  per 100  $\text{cm}^2$  (Nicosia, et al., 2009). Activity within contaminated areas can re-suspend the methamphetamine into the air thereby making inhalation possible (VanDyke, et al., 2009). Exposure hazards exist from the chemicals used in the synthesis and from the air-born final product.

Often, first responders such as fire, emergency medical or law enforcement personnel discover these clandestine methamphetamine labs. In these situations, the personal protective equipment worn by these first responders may not provide adequate protection against methamphetamine and the hazardous chemicals used in its synthesis. When evaluating Hazardous Substances Emergency Events Surveillance data (HSEES) collected by the Agency for Toxic Substances and Disease Registry (ATSDR) between 2001 and 2008, Melnikova *et al.* found that 61% of the victims treated for exposure symptoms from clandestine methamphetamine labs were first responders (Melnikova, et al., 2011). Respiratory irritation was the symptom reported by the majority of victims, followed by headache, chemical burns, eye irritation, gastrointestinal problems and dizziness/central nervous system effects (Melnikova, et al., 2011).

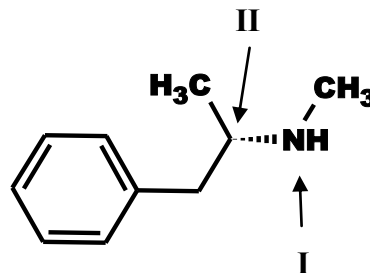
experiments in this study, methamphetamine hydrochloride was dissolved in methanol (25% w/v) and then mixed in a 1:1 ratio with 7 N sodium hydroxide (NaOH). After addition of NaOH and mixing, an oil layer assumed to be the 100% free base, formed. All analyses were performed using this free base.

### Methamphetamine hydrochloride



Structure 1

### Methamphetamine



Structure 2.

Hydroxyl radicals, which are among the primary oxidizing radicals in the indoor environment, (Sarwar, et al., 2002; Sexton, et al., 2004; Weschler and Shields, 1996; 1997) were generated from the photolysis of methyl nitrite (CH<sub>3</sub>ONO) in the presence of nitric oxide (NO) in air. (Atkinson, et al., 1981) CH<sub>3</sub>ONO was prepared in gram quantities using the method of Taylor *et al.* (Taylor, et al., 1980) and stored in a lecture bottle at room temperature. The CH<sub>3</sub>ONO purity (>95%) was verified by GC/MS.

Ozone was produced by photolyzing air with a mercury pen lamp in a separate Teflon chamber. Aliquots of this O<sub>3</sub>/air mixture were added to the Teflon reaction chamber using a gas-tight syringe.

All compounds, with the exception of methamphetamine were used as received and had the following purities: Sigma-Aldrich (Milwaukee, WI): terpinolene (90%), limonene (99%), acetonitrile (>99 %), O-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine hydrochloride (PFBHA) (98+%); Fisher Scientific (Fairlawn, NJ): methanol (99%), sodium hydroxide micro pearls; Spectrum Analytical (New Brunswick, NJ): Nitric oxide (99+% pure) was obtained as a 4942 ppm mixture in nitrogen from Butler Gases (Morrisville, PA). Helium (UHP grade), the carrier gas, was supplied by Amerigas (Sabraton, WV). Experiments were carried out at (297 ± 3) K and 1 atmosphere pressure.

### 1.2 Experimental Apparatus

Experiments to measure the gas-phase rate constant of the OH· + methamphetamine (Structure 2) reaction were conducted with an apparatus described here. (Atkinson, et al., 1981; Orji and Stone, 1992; Veillerot, et al., 1996; Williams, et al., 1993) Reactants were introduced and samples were withdrawn through a 6.4-mm Swagelok fitting attached to a 40 - 60 L Teflon film chamber. Compressed air from the National Institute for Occupational Safety and Health (NIOSH) facility was passed through anhydrous CaSO<sub>4</sub> (Drierite, Xenia, OH) and molecular sieves (Drierite, Xenia, OH) to remove both moisture and organic contaminants. This dry compressed air was added as a diluent to the reaction chambers and the fill rate was controlled with a 0 - 100 L min<sup>-1</sup> mass flow controller (MKS, Andover, MA). Analysis of this purified air by gas chromatography/mass spectrometry revealed no quantifiable contaminants present in the ppb range. The filler system was equipped with a syringe injection port facilitating the introduction of both liquid and gaseous reactants into the chambers with the flowing air stream. All reactant mixtures were generated by this system. Irradiations were carried out in a light-tight chamber housing surrounding 5-mil FEP Teflon-film chambers (40 - 60 L), which contained the following mix of lamps: six Philips TL40W/03; one GE F40BL; two QPANEL (Cleveland, OH) UV351 and seven QPANEL UV340. This lamp mixture approximates solar radiation from 300 to 450 nm.

### *1.3 Method Optimization*

Methamphetamine hydrochloride was first diluted in methanol to yield a 50% w/v solution. This methamphetamine solution was injected into the Teflon reaction chamber and gas-phase samples were taken using three SPME fibers, red (100 μm polydimethylsiloxane), black (75 μm carboxen-polydimethylsiloxane) and blue (65 μm polydimethylsiloxane-divinylbenzene). No quantifiable peaks were observed using the black (carboxen-PDMS) fiber.

A series of experiments were conducted to optimize volatilization for the work described here. Increasing the pH of a solution increases the likelihood that the protonated compound will de-protonate forming its free-base (volatile) form. When the solution pH equals the compounds pK<sub>a</sub>, half of the molecules will be deprotonated. Further increases of the pH will allow the solution to accept additional protons from the compound, thereby increasing the concentration of the free-base form of the

methamphetamine. Ratios of the 100% methamphetamine:7N ammonia were varied from 9:1 to 1:1 to determine the optimal ratios for volatilization of methamphetamine. The ratio that gave the highest instrument response in peak area counts was 1:1. The PDMS coated fiber (red) has a higher affinity for hydrophobic compounds such as the methamphetamine free-base and resulted in peak areas 3.5 times greater than those sampled with the mid-polarity PDMS-DVB fiber (blue). As a result of these experiments, the PDMS coated fiber was utilized in all of the experiments described here.

After determining ratios and selecting the appropriate SPME fiber, sodium hydroxide (strong base) and ammonia (weak base) were compared to further optimize volatilization and increase peak area. A 25% w/v methamphetamine/methanol solution was made fresh weekly. From that, fifty  $\mu\text{L}$  of the 25% w/v methamphetamine hydrochloride solution was injected through the septa of a 40 mL VOC vial. A red SPME fiber was exposed to the headspace in the vial and immediately analyzed and integrated. Next, 50  $\mu\text{L}$  of the 25% w/v methamphetamine hydrochloride solution and 50  $\mu\text{L}$  of 7N ammonia were injected into a 40 mL vial, the contents were vortexed for approximately 15 seconds and the red SPME fiber was exposed for 1 minute to the headspace in the vial then immediately analyzed. This procedure was repeated using 50  $\mu\text{L}$  of 7M sodium hydroxide. When the peak areas of the deprotonated samples were compared with the area of the salt head space sample, the increase of 7N  $\text{NH}_3$  peak area was 140 times that of methamphetamine only and the 7M NaOH peak area was 970 times greater. The 100% methamphetamine/7M NaOH procedure was replicated 10 times. The average increase in peak area counts was 900 fold from samples of methamphetamine/NaOH mixture compared to methamphetamine only. The rapid conversion of methamphetamine HCl to the free-base using the NaOH increases the vaporization of the free-base and allows for rapid SPME sampling in the gas-phase.

From these experiments the optimal experimental parameters were determined to be a 1:1 ratio of the 100% methamphetamine hydrochloride solution:7M sodium hydroxide for extraction of the methamphetamine free base and a red (PDMS) SPME fibers for gas-phase sampling.

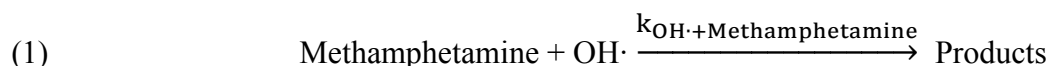
#### *1.4 Kinetics*

All reaction kinetic samples were quantitatively monitored using an Agilent (Palo Alto, CA) 6890 gas chromatograph with a 5973 mass selective detector and a flame ionization detector (GC/MS/FID) and

Agilent ChemStation software. Samples were collected using a 100  $\mu\text{m}$  polydimethylsiloxane SPME fiber assembly (Supelco, Milwaukee, WI) that was inserted into a 6.4 mm Swagelok fitting attached to the 45 L Teflon-film bag. The SPME fiber was exposed for 5 minutes within the chamber, and then inserted into the injector of the Agilent 6890 gas chromatograph. Compound separation was achieved using a Restek (Bellefonte, PA) Rtx-1701 (30 m long, 0.53 mm i.d., 1  $\mu\text{m}$  thickness) column. The GC temperature program used was: injection port 250  $^{\circ}\text{C}$ ; initial oven temperature 33  $^{\circ}\text{C}$  for 5 minutes; ramp 12  $^{\circ}\text{C}/\text{minute}$  to 240  $^{\circ}\text{C}$  final temperature and held for 2 minutes. The Agilent 5973 mass selective detector was tuned using perfluorotributylamine (FC-43). Full-scan electron impact (EI) ionization spectra were collected from  $m/z$  35 to 650. Preliminary compound identifications from the Agilent 6890/5973 GC/MS data sets were made by searching the NIST 98 Mass Spectral Library.

Experiments to measure the gas-phase reaction rate constant of  $\text{O}_3$  with methamphetamine were conducted using a similar chamber as described above, but the ozone concentration was measured using a UV photometric ozone analyzer (Thermo Environmental model 49-i Franklin, MA). An additional port was added to the Teflon chamber to facilitate the injection of  $\text{O}_3$ .

The experimental procedures for determining the methamphetamine +  $\text{OH}\cdot$  reaction kinetics were similar to those described previously. (Bradley, et al., 2001; Wells, 2004; Wyatt, et al., 1999)



The rate equations for reactions 1 and 2 are combined and integrated, resulting in the following equation:

$$(3) \quad \ln \left( \frac{[\text{Methamphetamine}]_0}{[\text{Methamphetamine}]_t} \right) = \frac{k_{\text{OH}\cdot+\text{Methamphetamine}}}{k_{\text{Ref}}} \ln \left( \frac{[\text{Ref}]_0}{[\text{Ref}]_t} \right)$$

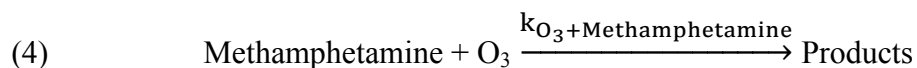
If reaction with  $\text{OH}\cdot$  is the only removal mechanism for methamphetamine and reference, a plot of  $\ln([\text{methamphetamine}]_0/[\text{methamphetamine}]_t)$  versus  $\ln([\text{Ref}]_0/[\text{Ref}]_t)$  yields a straight line with an intercept of zero. Multiplying the slope of this linear plot by  $k_{\text{Ref}}$  yields  $k_{\text{OH}\cdot+\text{methamphetamine}}$ . The  $\text{OH}\cdot$  rate constant



experiments for methamphetamine employed the use of two reference compounds: limonene and terpinoline. The use of two different reference compounds with different OH· rate constants aids to ensure the accuracy of the methamphetamine/OH· rate constant and demonstrates that other reactions are not removing methamphetamine.

For the methamphetamine/OH· kinetic experiments the typical concentrations of the pertinent species in the 40 - 60 L Teflon chamber were 1.7 – 3.0 ppm ( $4.2 - 7.4 \times 10^{13}$  molecule  $\text{cm}^{-3}$ ) methamphetamine, 1.7 – 3.3 ppm ( $4.2 - 8.1 \times 10^{13}$  molecule  $\text{cm}^{-3}$ ) reference, 10 ppm ( $2.5 \times 10^{14}$  molecule  $\text{cm}^{-3}$ ) CH<sub>3</sub>ONO, and 0.6 ppm ( $1.5 \times 10^{13}$  molecule  $\text{cm}^{-3}$ ) NO in air. The gas-phase mixtures were allowed to reach equilibrium before initial species concentration ( $[X]_0$ ) samples were collected. Typically, three photolysis intervals of 5 to 10 seconds each were used on the reaction mixture for a combined total photolysis time of approximately 20 –25 seconds. The peak area from the total ion chromatogram (TIC) from the Agilent 5973 mass selective detector was used to determine methamphetamine and reference concentrations.

The experimental procedures for the determination of the methamphetamine + O<sub>3</sub> reaction kinetics were similar to those described previously. (Atkinson and Aschmann, 1984)



The methamphetamine/O<sub>3</sub> rate constant was determined using a pseudo-first-order technique where the concentration of methamphetamine was effectively held constant in relation to the O<sub>3</sub> concentration. This allowed the O<sub>3</sub> to decay in a first-order manner (Espenson, 1995). Ozone was injected into the reaction chamber as it was being filled with air and methamphetamine. Assuming a 100% conversion of methamphetamine HCl to the free-base, the range of methamphetamine concentrations inside the Teflon chamber was 0.56 – 1.67 ppm ( $1.4 - 4.1 \times 10^{13}$  molecule  $\text{cm}^{-3}$ ). The additions of O<sub>3</sub> in the chamber resulted in an O<sub>3</sub> chamber concentration of 0.073 – 0.087 ppm ( $0.18 - 0.21 \times 10^{13}$  molecule  $\text{cm}^{-3}$ ). The chamber was connected within 5 seconds to the Thermo Electron UV photometric ozone analyzer Model 49i and ozone concentration measurements integrated over 10 second

time intervals were collected up to a total of 600 seconds. Methamphetamine did interfere with the absorbance signal at 254nm. To overcome this, experiments were performed at all concentration levels with and without ozone and the interference background was subtracted. The plot of the uncorrected data can be seen in the supplemental information.

Methamphetamine and each of the reference compounds were injected into separate Teflon chambers and the peak area was monitored over a period of several hours. No changes in peak area were noted, therefore, wall losses in these experiments were determined to be negligible.

To determine possible chromatographic interferences from reference/OH $\cdot$  reaction products, both methamphetamine and the reference compounds were reacted with the OH $\cdot$  radical in separate experiments and analyzed as described previously. (Wells, 2004) No chromatographic interferences were observed. All measurements were duplicated. A relative standard deviation of 3.4% was achieved with the described sampling methods utilizing the Agilent 6890/5973 GC/MS system (Wells, 2004).

### *1.5 Reaction Product Studies*

Identification of reaction products was made using O-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine (PFBHA) to derivatize carbonyl products. (Fick, et al., 2003; Yu, et al., 1998) Experimental methods for reaction product identification were similar to methods used for kinetic experiments, except the reference compound was excluded from the reaction mixture. An additional port was added to the Teflon chamber to facilitate the injection of ozone.

Derivatized reaction products were analyzed using a Varian (Palo Alto, CA) 3800/Saturn 2000 GC/MS system operated in both the EI and CI modes. (Yu, et al., 1998) Compound separation was achieved by a J&W Scientific (Folsom, CA) DB-5MS (0.32 mm i.d., 30-m long, 1  $\mu$ m film thickness) column and the following GC oven parameters: 60  $^{\circ}$ C for 1 minute then 20  $^{\circ}$ C/min to 170  $^{\circ}$ C, then 3  $^{\circ}$ C/min to 280  $^{\circ}$ C and held for 5 minutes.

Samples were injected in the splitless mode, and the GC injector was returned to split mode one minute after sample injection, with the following injector temperature parameters: 60  $^{\circ}$ C for 1 minute then 180  $^{\circ}$ C/min to 250  $^{\circ}$ C and held to the end of the chromatographic run. (Yu, et al., 1998) The Saturn 2000

ion trap mass spectrometer was tuned using FC-43. Full-scan EI ionization spectra were collected from  $m/z$  40 to 650. Acetonitrile was the chemical ionization reagent used for all CI spectra. When possible, commercially available samples of the identified products were derivatized and subsequently analyzed to verify matching ion spectra and chromatographic retention times. Derivatized chromatographs were compared to background chromatographs and peaks to determine product peaks.

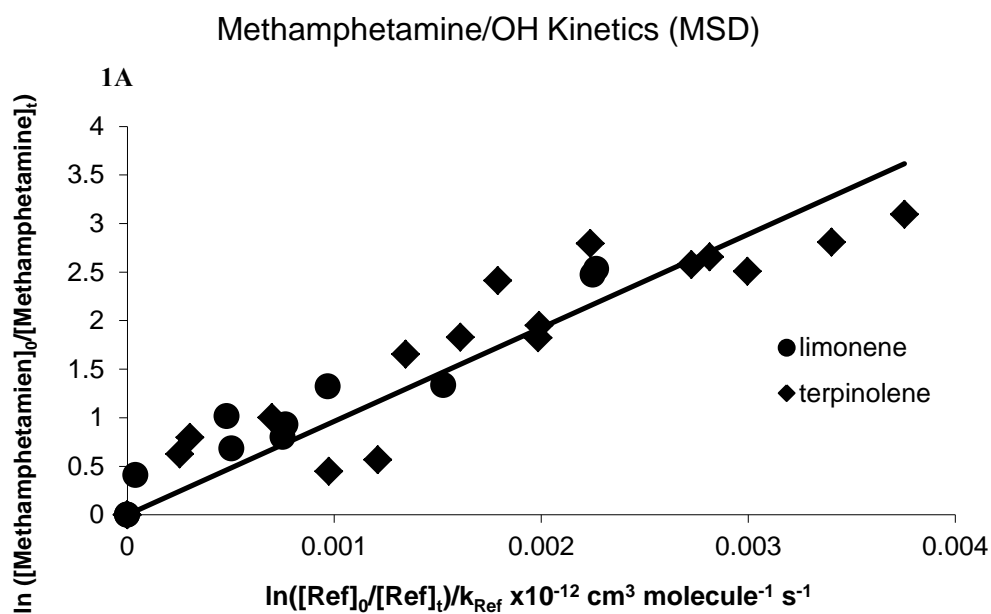
Derivatization of the carbonyl reaction products was initiated by flowing 20 L of chamber contents at  $2.5 \text{ L min}^{-1}$  through an impinger containing 3.6 mL of methanol and 200  $\mu\text{L}$  of 0.02M PFBHA in acetonitrile to derivatize the carbonyl reaction products to oximes (Yu, et al., 1998) with minimal methanol evaporation during sample collection. The sample was removed from the impinger and allowed to sit for a 24 to 48 hour time period in the dark. The reacted solutions were gently blown to dryness with UHP  $\text{N}_2$ , reconstituted with 100  $\mu\text{L}$  of methanol, and then 1  $\mu\text{L}$  of the reconstituted solution was injected onto the Varian 3800/Saturn 2000 GC/MS system.

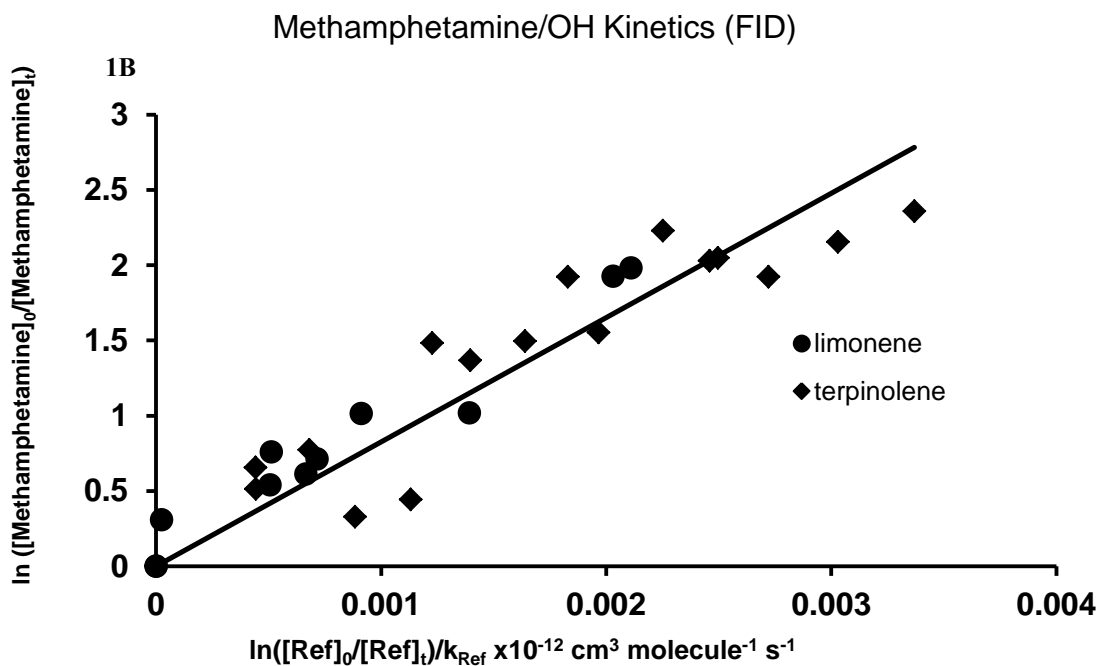
## 2. Results

### *Methamphetamine /OH· Reaction Rate Constant*

The OH· rate constant for methamphetamine (Structure 2) was obtained using the relative rate method described above. The plot of a modified version of equation (3) is shown in Figure 1. The  $\ln([\text{Ref}]_0/[\text{Ref}]_t)$  term is divided by the respective reference rate constant (limonene  $(164 \pm 41) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  and terpinolene  $(225 \pm 56) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ) (Atkinson, 1989; 1994; 2003; Bradley, et al., 2001) and multiplied by  $10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , resulting in a unitless number. This yields a slope that is equal to the OH·/methamphetamine rate constant,  $k_{\text{OH}+\text{methamphetamine}}$ , divided by  $10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . This modification allows for a direct comparison of the two reference compound/methamphetamine data sets. The slope of the line shown in Figure 1A yields an OH· bimolecular rate constant,  $k_{\text{OH}+\text{methamphetamine}}$ , of  $(960 \pm 100) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  measured by integrating the area under the chromatographic peak. The plot in Figure 1B was obtained by integrating the FID data and a bimolecular rate constant,  $k_{\text{OH}+\text{methamphetamine}}$ , of  $(830 \pm 90) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  was measured. The data points at the origin are experimental points because pre-irradiation,  $t = 0$ , data showed no detectable loss of methamphetamine or reference. The error in the rate constant stated above is

the 95% confidence level from the uncertainty in the slope. Incorporating the uncertainties associated with the reference rate constants ( $\pm 25\%$  for limonene and terpinolene) used to derive the methamphetamine/ $\text{OH}\cdot$  rate constant yields a final value for  $k_{\text{OH}\cdot+\text{methamphetamine}}$ , of  $(960 \pm 100) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  for the MS data and  $(830 \pm 100) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  for the FID data (Atkinson, 1989; 1994; 2003). The methamphetamine/ $\text{OH}\cdot$  rate constant,  $k_{\text{OH}\cdot+\text{methamphetamine}}$ , has not been previously reported. The observed rate constant is an order of magnitude higher than the estimated  $k(\text{calc})_{\text{OH}\cdot+\text{methamphetamine}} = 92.6 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , calculated using the Environmental Protection Agency's rate constant calculation software, AOPWIN v1.91. (USEPA, 2000)

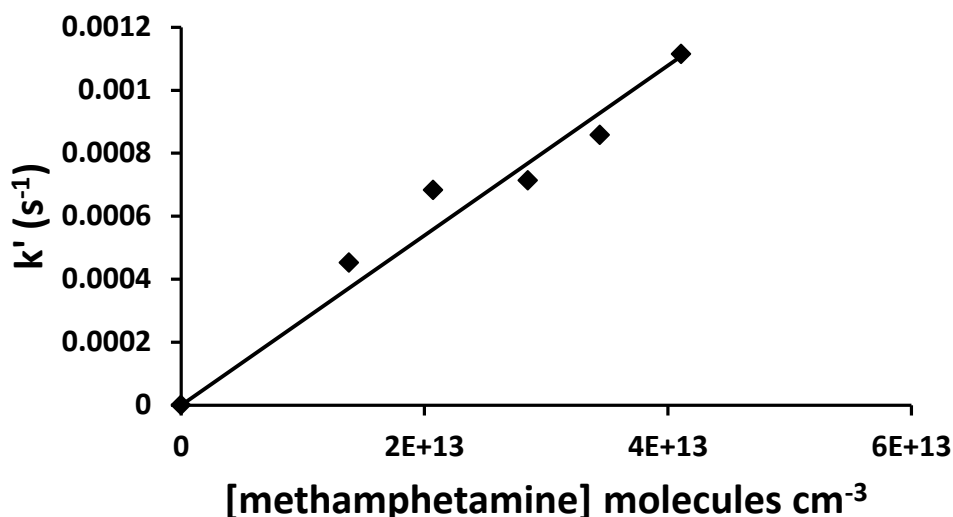




**Figure 1.** Methamphetamine relative rate plots with terpinolene ( ● ) and limonene ( ◆ ) as reference compounds. The measured OH· + methamphetamine rate constant using the GC/MS (Figure 1A),  $k_{\text{methamphetamine}+\text{OH}\cdot}$ , is  $(960 \pm 100) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  and  $(830 \pm 90) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  was measured using GC/FID (Figure 1B).

#### *Methamphetamine /O<sub>3</sub> Reaction Rate Constant*

The O<sub>3</sub> rate constant for methamphetamine (Structure 2) was measured using the pseudo-first-order techniques. The concentration of methamphetamine was assumed constant and the decay of O<sub>3</sub> was monitored. Figure 2 shows a plot of O<sub>3</sub> rate loss ( $k'$ ) as a function of methamphetamine concentration. The slope of the line is the bimolecular O<sub>3</sub> rate constant,  $k_{\text{O}_3+\text{methamphetamine}}$ ,  $(2.7 \pm 0.5) \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . The error in the rate constant above is the 95% confidence level from the variations in the slope. The methamphetamine/OH· rate constant,  $k_{\text{O}_3+\text{methamphetamine}}$ , has not been previously reported.

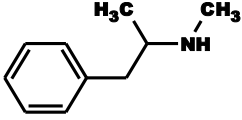
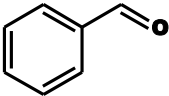
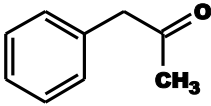
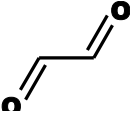
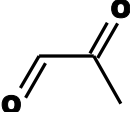


**Figure 2.** Methamphetamine pseudo-first-order rate plot. The  $\text{O}_3 + \text{methamphetamine}$  rate constant,  $k_{\text{O}_3 + \text{methamphetamine}}$ , measured is  $(2.7 \pm 0.5) \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .

#### *Methamphetamine/OH· and Methamphetamine/O<sub>3</sub> Reaction Products*

The reaction products observed from the methamphetamine/OH· reaction (hydrogen abstraction or OH· addition) are listed in Table 1. The methamphetamine/OH· products observed and positively identified using the pure compound for verification by derivatization were: benzaldehyde, ethanedial (glyoxal), and 2-oxopropanal (methylglyoxal). Structures and ions used to identify these compounds are listed in Table 1. Elucidation of the other major reaction product, phenyl-2-propane, was facilitated by mass spectrometry of the derivatized reaction product coupled with plausible methamphetamine/OH· reaction mechanisms based on previously published volatile organic compound/OH· gas-phase reaction as described below (Atkinson, 1989; Bradley, et al., 2001; Smith, et al., 1992; Smith, et al., 1995; Veillerot, et al., 1996; Wallington, et al., 1993; Wells, 2004; Wells, et al., 1996; Wyatt, et al., 1999). An additional reaction product with a molecular mass of 146 amu was also observed.

**Table 1. Molecular Structure of Methamphetamine and Methamphetamine/OH· and Methamphetamine/O<sub>3</sub> Reaction Products**

Retention Time (minutes)	Name	Molecular Weight (amu)	Structure	CI Ions observed	HazAssess QSAR value <sup>a</sup>
	Methamphetamine	149			0.21
17.5	benzaldehyde	106		302	0.20
19.1 19.3	Phenyl-2-propanone (P2P)	134		330	0.10
24.9 25.2	Ethanedial* (glyoxal)	58		449	0.38
25.4	2-oxopropanal (methylglyoxal)	72		463	0.21

\*Observed from methamphetamine/OH· reaction only

<sup>a</sup> (Jarvis, et al., 2005)

The reaction products observed from the methamphetamine/O<sub>3</sub> addition are also listed in Table 1. The methamphetamine/O<sub>3</sub> products observed and positively identified using the pure compound for verification by derivatization were: benzaldehyde, ethanedial (glyoxal), and 2-oxopropanal (methylglyoxal). Structures and ions used to identify these compounds are listed in Table 1. Elucidation of the other major reaction product, phenyl-2-propane, was facilitated by mass spectrometry of the derivatized reaction product coupled with plausible methamphetamine/O<sub>3</sub> reaction mechanisms based on previously published volatile organic compound /O<sub>3</sub> gas-phase reaction as described below (Atkinson, 1989; Bradley, et al., 2001; Smith, et al., 1992; Smith, et al., 1995; Veillerot, et al., 1996; Wallington, et al., 1993; Wells, 2004; Wells, et al., 1996; Wyatt, et al., 1999).

Derivatization of nonsymmetric carbonyls using PFBHA typically resulted in multiple chromatographic peaks due to geometric isomers of the oximes. Identification of multiple peaks of the same oxime compound is relatively simple since the mass spectra for each chromatographic peak of a

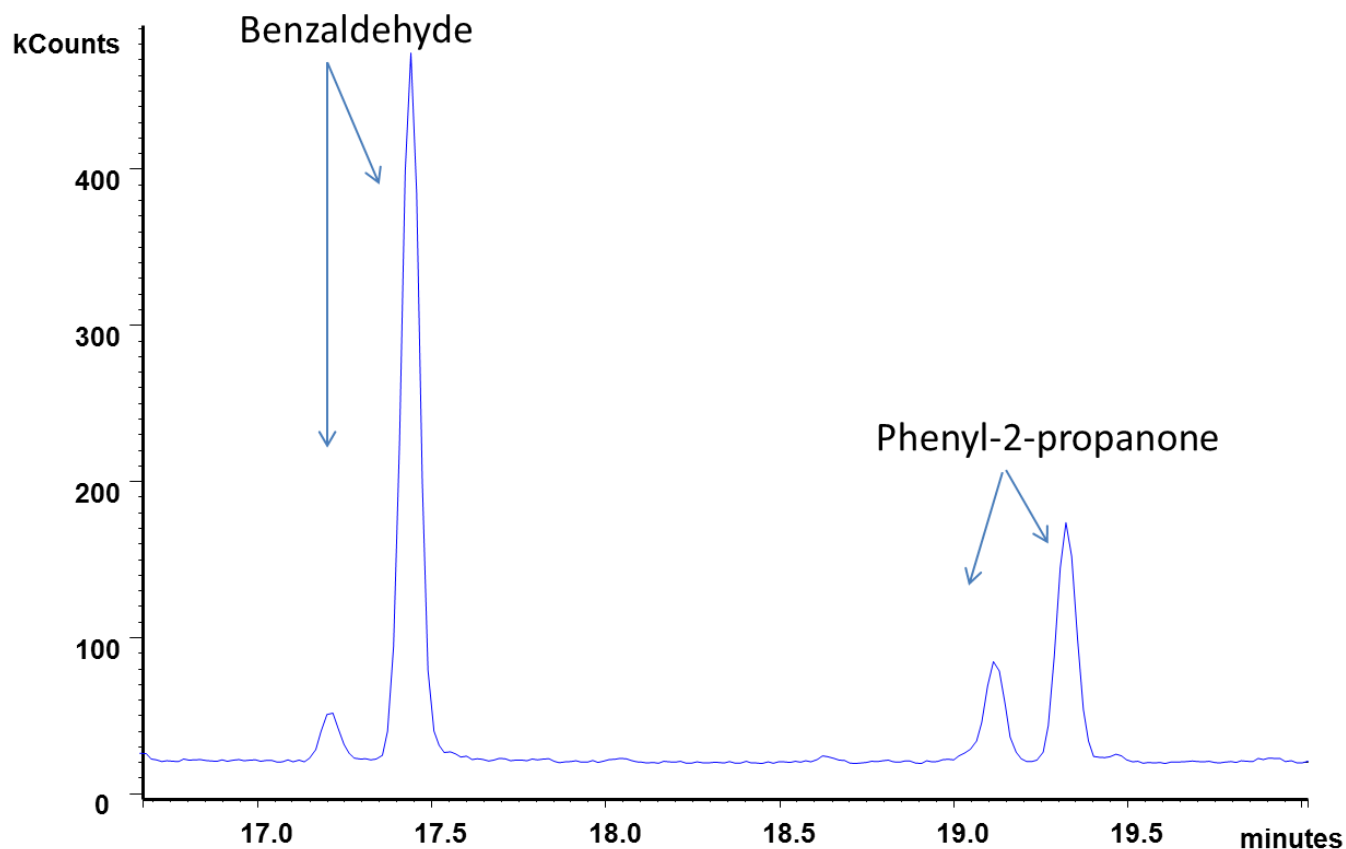
particular oxime are almost identical. Typically, the PFBHA-derivatized oximes' (generic structure:  $F_5C_6CH_2ON=C(R_1)(R_2)$ ) mass spectra included an ion at  $m/z$  181 ( $[CH_2C_6F_5]^+$  fragment) with a large relative intensity (>40%) and a  $[PFBHA \text{ oxime} + 181]^+$  ion (due to reactions in the ion trap mass spectrometer) (Yu, et al., 1998). In most cases, the  $m/z$  181 ion relative intensity for the chromatographic peaks due to methamphetamine/ $OH\cdot$  and methamphetamine/ $O_3$  reaction product oximes was either the largest or one of the largest in the mass spectrum and was used to generate selected ion chromatograms (Yu, et al., 1998).

The following describe in chronological retention time order the mass spectra data for the individual reaction products observed utilizing PFBHA derivatization and the Varian 3800/Saturn 2000 GC/MS system. The reaction products' chromatographic peak areas were a function of the initial methamphetamine concentration and were observed only after  $OH\cdot$  initiation or addition of  $O_3$  to the methamphetamine chamber contents. Derivatization experiments performed in the absence of methamphetamine, but in the presence of all other chemicals in the reaction chamber (methanol/methyl nitrite/ $NO$ /air) did not result in any of the data reported below except for small amounts of 2-oxopropanal and ethanedial which were < 2% of the derivatized peak area. However, 2-oxopropanol and ethanedial oxime peak areas increased with methamphetamine/ $OH\cdot$  or methamphetamine/ $O_3$  reaction initiation, indicating that they are likely products of the methamphetamine/ $OH\cdot$  and methamphetamine/ $O_3$  reactions.

#### *Benzaldehyde ( $C_6H_5CH=O$ )*

The chromatographic peaks for the oxime observed at 17.2 and 17.4 minutes were observed as a reaction product of methamphetamine/ $OH\cdot$  had ions at  $m/z$  (relative intensity) 301 (100%), 181 (74%), 271 (58%), 65 (29%) and 89 (27%). Using acetonitrile for chemical ionization, an  $M+1$  ion of  $m/z$  of 302 was observed for the PFBHA-derivatized sample. The PFBHA-benzaldehyde oxime was synthesized to confirm this chromatographic assignment. A chromatograph showing this reaction product can be seen in Figure 3. This carbonyl compound was also observed as a methamphetamine/ $O_3$  reaction product.

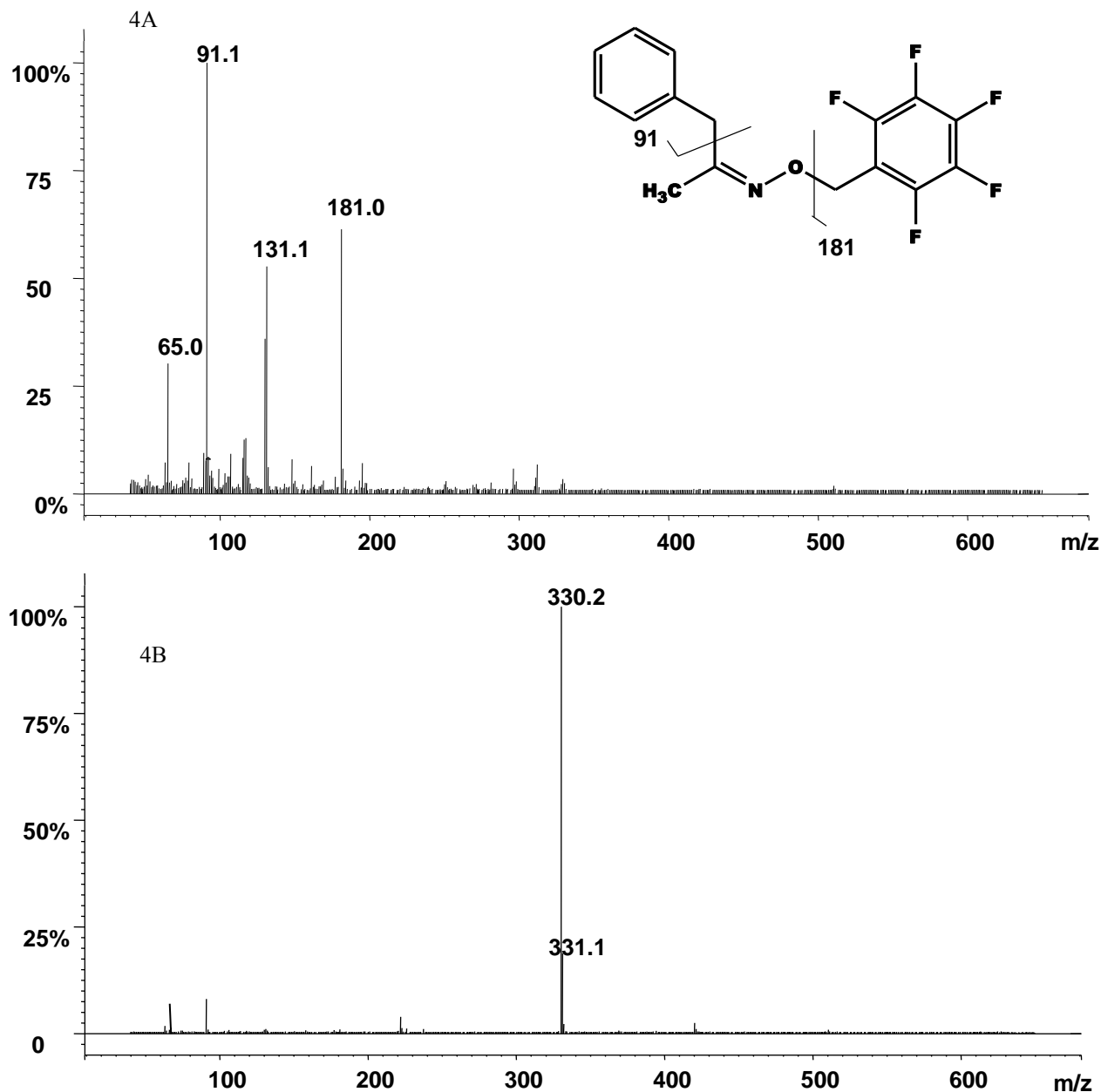




**Figure 3.** Chromatograph of main derivatized products benzaldehyde (two peaks: 17.25 and 17.45 minutes) and phenyl-2-propanone (2 peaks: 19.1 and 19.3 minutes) from  $\text{OH}\cdot$  + methamphetamine reaction.

*Phenyl-2-propanone* ( $\text{C}_6\text{H}_5\text{CH}_2\text{C}(=\text{O})\text{CH}_3$ )

The chromatographic peaks for the oxime observed at 19.1 and 19.3 minutes were observed as a reaction product of methamphetamine/ $\text{OH}\cdot$  had ions at  $m/z$  (relative intensity) 91 (100%), 181 (67%), 131 (52%), 130 (36%) and 65 (30%) as seen in Figure 4A. Using acetonitrile for chemical ionization, an  $M+1$  ion of  $m/z$  of 330 was observed for the PFBHA-derivatized sample (Figure 4B). A chromatograph showing this reaction product can be seen in Figure 3. This carbonyl compound was also observed as a methamphetamine/ $\text{O}_3$  reaction product.



**Figure 4.** PFBHA derivatized product of methamphetamine oxidation by OH $\cdot$  (19.1 minutes) A) electron ionization spectrum MW = 329 amu B) acetonitrile chemical ionization spectrum MW = 330 amu.

*Ethanedial (Glyoxal, HC(=O)C(=O)H)*

The chromatographic peaks for the oxime observed at 24.4 and 25.2 minutes were observed as a reaction product of methamphetamine/OH $\cdot$  and had ions at  $m/z$  (relative intensity) 181 (100%) and 448 (17%). The  $m/z$  448 ion is the result of a double PFBHA derivatization indicating a reaction product with

a molecular weight of 58. Using acetonitrile for chemical ionization, an M+1 ion of  $m/z$  of 449 was observed for the PFBHA-derivatized sample. The PFBHA-glyoxal oxime was synthesized to confirm this chromatographic assignment. This carbonyl compound was also observed as a methamphetamine/ $O_3$  reaction product.

#### *2-Oxopropanal (Methylglyoxal, $CH_3C(=O)C(=O)H$ )*

The chromatographic peaks for the oxime observed at 25.2 and 25.4 minutes were observed as a reaction product of methamphetamine/ $OH\cdot$  and had ions at  $m/z$  (relative intensity) 181 (100%) and 265 (28%). The  $m/z$  462 ion is the result of a double PFBHA derivatization indicating a reaction product with a molecular weight of 72. Using acetonitrile for chemical ionization, an M+1 ion of  $m/z$  of 463 was observed for the PFBHA-derivatized sample. The PFBHA-methylglyoxal oxime was synthesized to confirm this chromatographic assignment and the second chromatographic peak for PFBHA-methylglyoxal overlaps slightly with the 25.2 minute peak of PFBHA-glyoxal. This carbonyl compound was also observed as a methamphetamine/ $O_3$  reaction product.

## **Discussion**

$OH\cdot$  reacts with methamphetamine by H-atom abstraction or  $OH\cdot$  addition to the carbon-carbon double bonds (Atkinson, 1989; Atkinson and Aschmann, 1993; Murphy, et al., 2007). The reactive structure of methamphetamine can be drawn as shown in Structure 2. The sites labeled I and II identified in Structure 2 contribute approximately 95%, to the calculated methamphetamine/ $OH\cdot$  rate constant of  $92.6 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (USEPA, 2000) which is an order of magnitude slower than the averaged measured value reported here  $(960 \pm 100) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .

Ozone reacts with alkenes by addition to the carbon-carbon double bond (Criegee, 1975) and with amines through electron transfer reactions (Bailey, et al., 1972). Ozone reactions with methamphetamine should primarily be electron transfer reactions, reactions of ozone with the phenyl ring are not anticipated. This assumption is based on published  $O_3$  rate constants of compounds containing aromatic rings such as benzene and alkyl benzene compounds have reaction rates of  $< 1 \times 10^{-20} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , (Atkinson,

2003). The measured value reported here  $(2.7 \pm 0.5) \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  has not been previously reported.

For the methamphetamine/OH $\cdot$  reaction the experimental parameters were set to minimize other side reactions and highlight the primary OH $\cdot$  hydrogen abstraction and OH $\cdot$  addition step. The methamphetamine concentration was kept low and the photolysis times were as short as possible. Additionally, nitric oxide (NO) was added to facilitate the generation of OH $\cdot$  and to minimize O $_3$  and NO $_3\cdot$  radical formation preventing other possible radical reactions. The possible mechanistic steps leading to product formation are described below.

### *Benzaldehyde*

The methamphetamine/OH $\cdot$  reaction mechanism leading to the formation of benzaldehyde (C $_6$ H $_5$ CH=O) likely occurs through hydrogen abstraction of the hydrogen on the carbon adjacent to the secondary amine (Site I, Structure 2), producing the radical, C $_6$ H $_5$ CH $_2$ CH(CH $_3$ )N $\cdot$ CH $_3$ . Subsequent addition of oxygen to the radical and a hydrogen-shift leads to decomposition and formation of the peroxyradical, C $_6$ H $_5$ CH $_2$ OO $\cdot$  and the radical CH $_3$ NHC $\cdot$ H(CH $_3$ ). The (CH $_3$ ) $_2$ COO $\cdot$  peroxyradical can then react with NO to form NO $_2$  and benzaldehyde. Benzaldehyde product formation from the methamphetamine/O $_3$  reaction begins with an electron transfer reaction at the amine and then follows a similar mechanistic pathway to that of the methamphetamine/OH $\cdot$  reaction. A proposed reaction scheme detailing both the OH $\cdot$  and O $_3$  reactions can be seen in Figure 5.

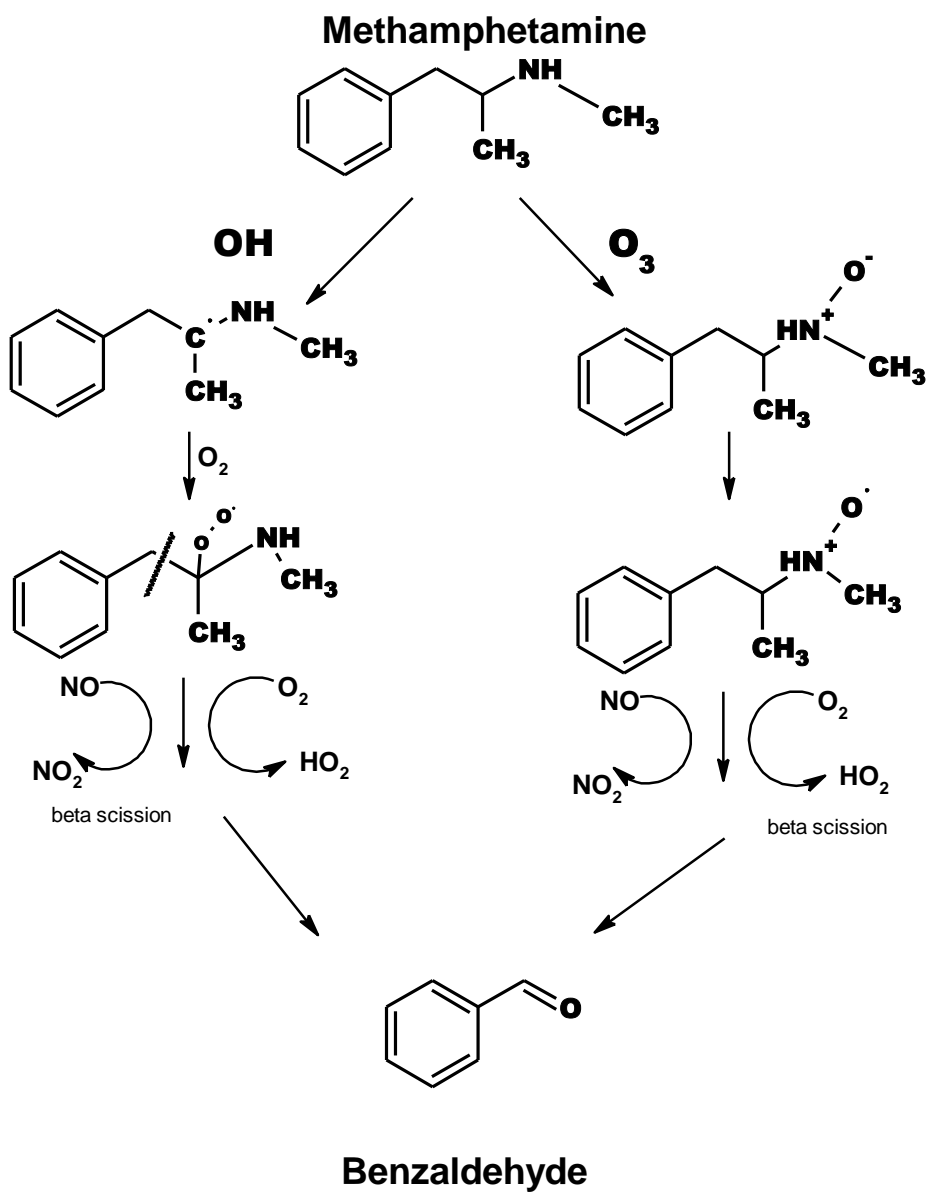


Figure 5. Proposed Mechanism for the formation of Benzaldehyde from Methamphetamine reactions with  $\text{OH}\cdot$  and  $\text{O}_3$ .

### *Phenyl-2-propanone*

OH· can react with methamphetamine by abstraction of the hydrogen at site I of Structure 2, producing the radical C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>CH(CH<sub>3</sub>)N·CH<sub>3</sub>. Subsequent addition of oxygen to the radical and a hydrogen-shift leads to decomposition and formation of the peroxyradical, C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>CH(CH<sub>3</sub>)OO· and the radical CH<sub>3</sub>N·(H). The CH<sub>2</sub>(OH)CHOO· radical can then react with NO to form NO<sub>2</sub> and phenyl-2-propanone. Phenyl-2-propanone product formation from the methamphetamine/O<sub>3</sub> reaction begins with an electron transfer reaction at the amine, and then follows a similar mechanistic pathway to that of the methamphetamine/OH· reaction.

The reaction product methylglyoxal appears in both the methamphetamine/OH· and the methamphetamine/O<sub>3</sub> reactions. Ozone/alkene reactions can produce steady state OH· concentrations which would explain the observation of these products in both reactions (Paulson, et al., 1999). However, addition of a large concentration of cyclohexane (628 ppm) to scavenge OH· in the methamphetamine/O<sub>3</sub> reaction mixture effectively eliminates the methamphetamine/OH· side-reaction.

The reaction product glyoxal is only observed as a reaction product from methamphetamine/OH· reactions and is most likely formed as a product of secondary reactions in the gas-phase.

Product experiments were conducted to determine if relative humidity had an effect on the methamphetamine reactions. The Teflon chamber was filled as in previously described experiments using a filler system equipped with a humidification chamber. The relative humidity was set to 50%. Identical derivatization procedures were followed and the data from the <5% and 50% samples were compared. There were no differences in products formed in either OH· or O<sub>3</sub> reactions with methamphetamine.

The Chemical Asthma Hazard Assessment Program developed by Jarvis et al. (Jarvis, et al., 2005) was used to calculate a Hazard Index of the observed oxygenated organic reaction products. The Hazard Index is a value between 0 and 1 determined by comparing the substructures of the chemical of interest against a database of substructures present in known occupational respiratory sensitizers. While the program results should not be used definitively, the closer the Hazard Index is to 1 the stronger the prediction is that the submitted compound has the potential to be a respiratory sensitizer. Both the methamphetamine and its oxygenated organic products were evaluated using this tool and the results are

presented in Table 1. Only one product, phenyl-2-propanone has a lower HazAssess value than that of methamphetamine. This suggests that the gas-phase products could play an equal or more adverse role in terms of health effects than the parent compound.

## Conclusions

To investigate the detailed gas-phase chemistry of methamphetamine (Structure 2), the hydroxyl radical reaction rate constant, ozone reaction rate constant and respective reaction mechanisms were investigated. The OH· can react by either abstract hydrogen or addition to the carbon-carbon double bond of methamphetamine. A bimolecular rate constant,  $k_{\text{OH}\cdot + \text{methamphetamine}}$ , of  $(960 \pm 100) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  was measured using the relative rate technique. This measured value is significantly faster than that predicted using AOPWIN software. Ozone reactions with methamphetamine occur through electron transfer reactions and a methamphetamine/O<sub>3</sub> rate constant,  $k_{\text{O}_3 + \text{methamphetamine}}$ , of  $(2.7 \pm 0.5) \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  was measured using pseudo-first order techniques.

The identification of the methamphetamine/OH· and methamphetamine/O<sub>3</sub> reaction products was facilitated by the use of derivatizing agent PFBHA. The reaction products benzaldehyde, glyoxal and methylglyoxal were positively identified using observed experimental data. The major reaction product, phenyl-2-propanone was proposed based on mass spectral data from PFBHA derivatization and previously published VOC/OH· and VOC/O<sub>3</sub> reaction mechanisms. The structures of the identified reaction products indicate that the hydrogen of the amine group plays an important role in the formation of reaction products in both the methamphetamine/O<sub>3</sub> and methamphetamine/OH· reactions.

Approximate indoor environment concentrations of the hydroxyl radical ( $1.23 \times 10^5$  molecules/cm<sup>3</sup>) and ozone ( $4.92 \times 10^{11}$  molecules/cm<sup>3</sup>) have been previously estimated by Sarwar (Sarwar, et al., 2002). Using the methamphetamine/OH· and methamphetamine/O<sub>3</sub> rate constants reported here pseudo-first order rate constants of 0.43 h<sup>-1</sup> and 0.60 h<sup>-1</sup> were determined, respectively. Comparing these values to a typical indoor air exchange rate of 0.6 h<sup>-1</sup>, suggests that the methamphetamine/O<sub>3</sub> reaction is expected to compete with air exchange as an indoor environment loss mechanism for methamphetamine (Wilson, et al., 1996).

The data and information from this study may be used by researchers developing clean-up procedures and final testing for remediation of methamphetamine. From the data here it is apparent that gas-phase reactions can produce reaction products and these reaction products may also pose potential health effects. It may also be possible to determine if methamphetamine was previously synthesized in a structure by testing for chemicals such as benzaldehyde and phenyl-2-propanone.

In addition, few studies exist that measure ozone-amine reaction rate constants. The data in the EPA AOPWIN database is insufficient to predict a reaction rate constant. Further investigations such as this should be completed to develop a QSAR database for this type of prediction.

Relative humidity may affect the formation of reaction products due to additional hydrolysis reactions. Also, the RH can have an effect on the rate of reaction, but, unless there is a significant sustained temperature increase accompanied by the increased humidity, the rate constant measured here would not be affected. The time involved in these experiments allows the air temperature in the chamber to be maintained at ambient conditions. The experimental results reported here were conducted under ambient conditions with <5% relative humidity. The purpose of this was to simulate real-world conditions with the exception of humidity. Product studies at 50% RH were conducted; however, the reaction products observed were the same as those in the <5% RH experiments. A more in-depth reaction product study using additional derivatization techniques might discover additional products.

No nitrogen containing products were found in the derivatization studies here. Unsuccessful attempts were made to derivatize the nitrogen using *N,O*-Bis(trimethylsilyl)trifluoroacetamide (BSTFA). Additional experiments using derivatization agents suitable for amines should be conducted to track the nitrogen products. Further studies should also be conducted to determine if aerosol particles are formed from these reactions which could explain the absence of gas-phase nitrogen containing products. These experiments could be conducted simultaneously using a denuder coated with a derivatization agent such as *N*-Methyl-*N*-(trimethyl-silyl)trifluoroacetamide (MSTFA) or *N,N*-Diethyltrimethyl-silylamine (TMSDEA) to capture gas-phase products and a filter pack for particulate capture.



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**Gas-Phase Reactions of Methamphetamine with Hydroxyl Radicals  
and Ozone**

**Crystal D. Forester  
Master's Thesis Supplemental Information**

**Committee Members:  
Dr. Suzanne Bell, Chair  
Dr. Harry Finklea  
Dr. Jonathan Boyd**

Hydroxyl Radical Kinetic data:

Chemical being studied	methamphetamine
Reference Compound	limonene
Reference Rate constant ( $10^{-12}$ ) =	1.64E+02

Date	5/15/2011
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	REF MSD	METH MSD	REF FID	METH FID
1/6/2011				
bkgd 11051502	462753	177211	3669110	2410624
bkgd 11051503	482327	217913	3775296	2706142
bkgd 11051504	473701	175633	3681565	2261954
bkgd 11051505	460773	238535	3610117	2902952
Std Dev	10054	31077	68365	288493
<b>RSD</b>	<b>0.02</b>	<b>0.15</b>	<b>0.02</b>	<b>0.11</b>

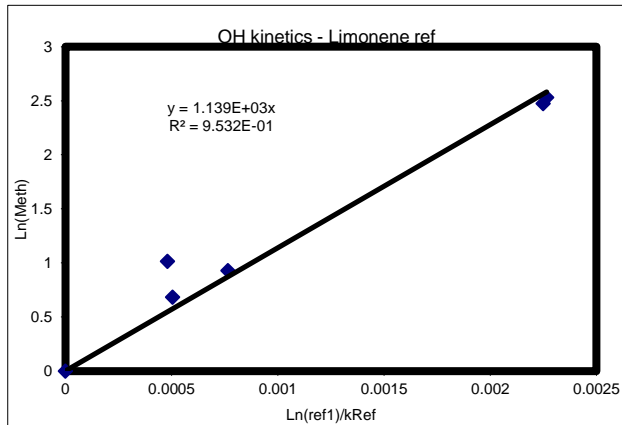
	MSD	FID
Avg [Ref 1] <sub>0</sub>	4.6989E+05	3.6840E+06
Avg [Chem] <sub>0</sub>	2.0232E+05	2.5704E+06

Photolysis time (sec)	10
-----------------------	----

phot 1 11051506	432576	102333	3389940	1496493
phot 1 11051507	414461	80052	3276372	1259367
phot 1 11051508	434285	73443	3387418	1201984

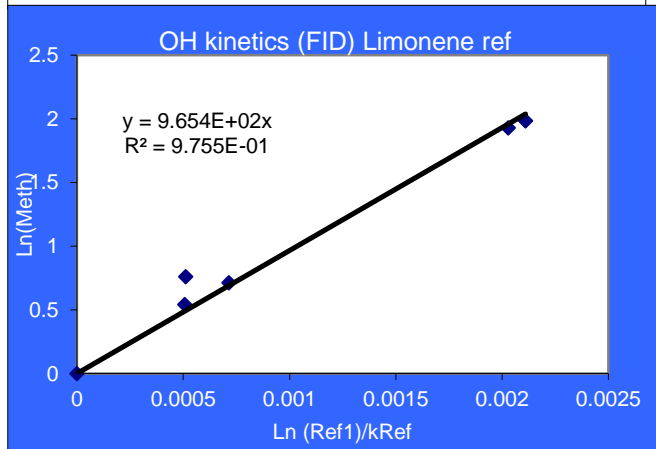
Photolysis time (sec)	10
-----------------------	----

phot 2 11051601	324931	17066	2606194	353722
phot 2 11051602	324053	16114	2640809	373807



MSD!!

Ln (Ref1)/kRef	Ln (Meth)
0	0
0.000504496	0.681633229
0.000765345	0.927189007
0.000480454	1.013355835
0.002249284	2.47277725
0.002265783	2.530176971



FID!!

Ln (Ref1)/kRef	Ln (Meth)
0	0
0.000507274	0.540944161
0.000715051	0.713459318
0.000511812	0.760095007
0.002110452	1.983312517
0.002029999	1.928084189

**Date** 5/16/2011

	REF MSD	METH MSD	REF FID	METH FID
Bkgd 11051701	955394	640339	6842391	6107322
Bkgd 11051702	799891	651287	5877508	6419191
Bkgd 11051703	553680	412418	4204585	4432475
Bkgd 11051804	958274	904464	6886302	8344727
Bkgd 11051805	819948	476811	5948431	4914978
Bkgd 11051806	817222	683317	5929330	6763885
Std dev	147478	172928	972128	1395851
RSD	<b>0.18</b>	<b>0.28</b>	<b>0.16</b>	<b>0.23</b>

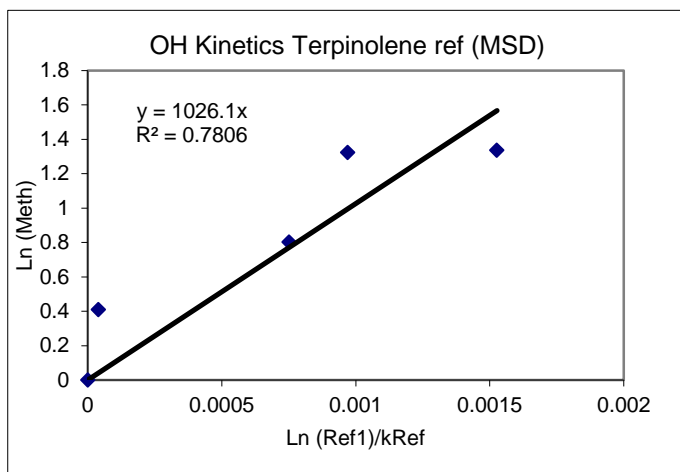
**MSD** Avg [Ref 1]<sub>0</sub> **8.1740E+05**  
**FID** Avg [Chem]<sub>0</sub> **6.2811E+05**

<b>Photolysis time (sec)</b>			<b>10</b>
------------------------------	--	--	-----------

Phot 1 11051807	722652	282135	5332442	3335321
Phot 1 11051808	811991	417339	5924711	4523713

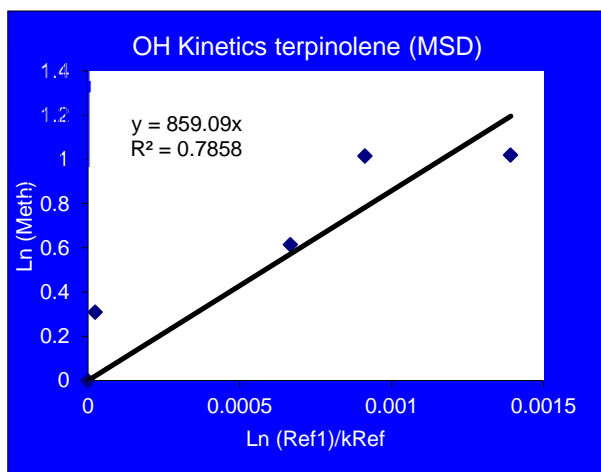
<b>Photolysis time (sec)</b>			<b>10</b>
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Phot 2 11051809	636310	165195	4734263	2224307
Phot 2 11051810	697207	167556	5121994	2235120



MSD!!

Ln (Ref1)/kRef	Ln (Meth)
0	0
0.000751236	0.800323262
0.000040	0.408810101
0.001527101	1.335582348
0.000969805	1.321391318



FID!!

Ln (Ref1)/kRef	Ln (Meth)
0	0
0.000666226	0.614118541
0.000024	0.309354351
0.001391733	1.019242061
0.000911747	1.01439255

OH Kinetics regression data for Limonene and Terpinolene (MSD):

0.0000 0.0000 SUMMARY OUTPUT

0.0005 0.6816

0.0008 0.9272

<i>Regression Statistics</i>	
Multiple R	0.9442
R Square	0.8916
Adjusted R Square	0.8876
Standard Error	0.3351
Observations	29.0000

0.0000 0.4088

0.0015 1.3356

ANOVA					
	<i>df</i>	<i>SS</i>	<i>MS</i>	<i>F</i>	<i>Significance F</i>
Regression	1.0000	24.9334	24.9334	222.0876	0.0000
Residual	27.0000	3.0313	0.1123		
Total	28.0000	27.9647			

0.0013 1.6538

0.0016 1.8283

0.0020 1.9505

	<i>Coefficients</i>	<i>Standard Error</i>	<i>t Stat</i>	<i>P-value</i>	<i>Lower 95%</i>	<i>Upper 95%</i>	<i>Lower 95.0%</i>	<i>Upper 95.0%</i>
Intercept	0.2522	0.0998	2.5273	0.0177	0.0474	0.4569	0.0474	0.4569
X Variable 1	850.4734	57.0688	14.902	0.0000	733.3779	967.568	733.377	967.568

0.0020 1.8212

0.0018 2.4111

0.0022 2.7941

std error (2sd) 114.1376

0.0000 0.0000

0.0012 0.5652

0.0010 0.4481

0.0007 0.9995

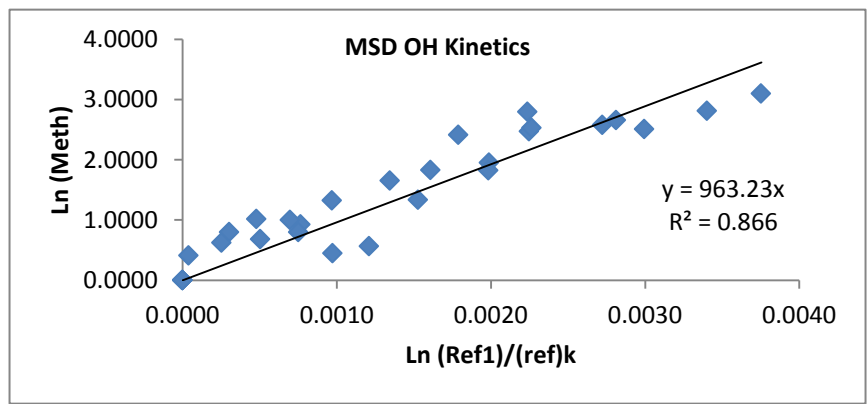
0.0027 2.5753

0.0030 2.5061

0.0028 2.6558

0.0038 3.0949

0.0034 2.8086



OH regression data for Limonene and terpinolene (FID):

SUMMARY OUTPUT

0.0000 0.0000  
 0.0005 0.5409  
 0.0007 0.7135  
 0.0005 0.7601  
 0.0021 1.9833  
 0.0020 1.9281  
 0.0000 0.0000  
 0.0007 0.6141  
 0.0000 0.3094  
 0.0014 1.0192  
 0.0009 1.0144  
 0.0003 0.2997  
 0.0000 0.0000  
 0.0004 0.6558  
 0.0004 0.5122  
 0.0014 1.3676  
 0.0016 1.4948  
 0.0020 1.5527  
 0.0012 1.4825  
 0.0018 1.9231  
 0.0023 2.2286  
 0.0000 0.0000  
 0.0011 0.4427  
 0.0009 0.3287  
 0.0007 0.7736  
 0.0025 2.0305  
 0.0027 1.9227  
 0.0025 2.0479  
 0.0034 2.3597  
 0.0030 2.1556

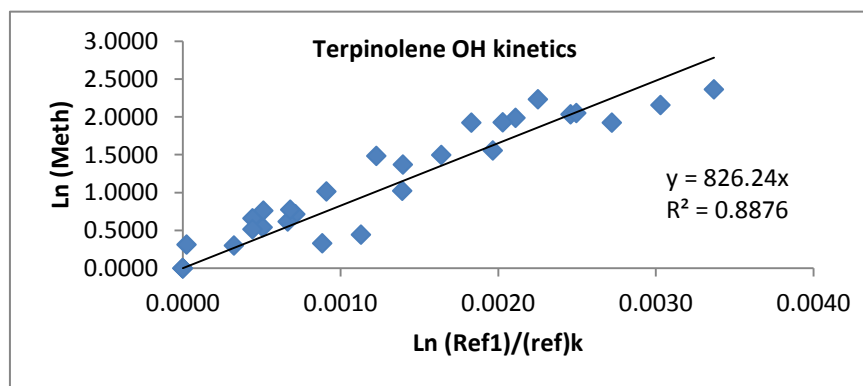
Regression Statistics	
Multiple R	0.9501
R Square	0.9027
Adjusted R Square	0.8992
Standard Error	0.2483
Observations	30.0000

ANOVA

	df	SS	MS	F	Significance F
Regression	1.0000	16.0120	16.0120	259.7714	0.0000
Residual	28.0000	1.7259	0.0616		
Total	29.0000	17.7378			

	Coefficients	Standard Error	t Stat	P-value	Lower 95%	Upper 95%	Lower 95.0%	Upper 95.0%
Intercept	0.1528	0.0733	2.0827	0.0465	0.0025	0.3030	0.0025	0.3030
X Variable 1	750.0405	46.5360	16.117	0.0000	654.7159	845.36	654.715	845.365

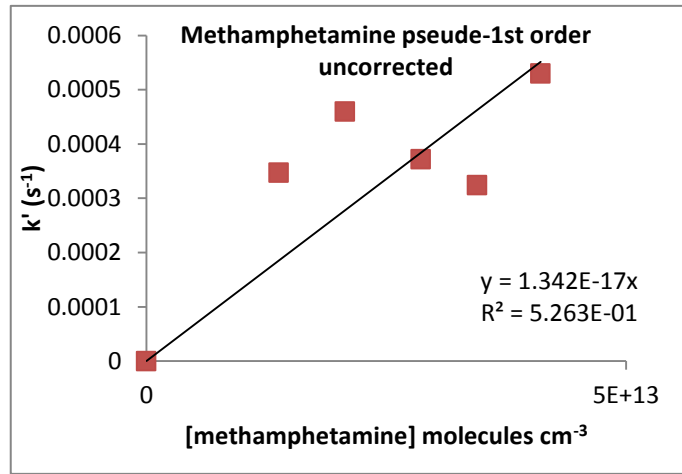
error (2sd) 93.0720





Pseudo-first order ozone kinetic plots uncorrected and background corrected:

[methamphetamine]		$k^1 s^{-1}$
[ppm]	[molec/cm <sup>-3</sup> ]	
0	0.00E+00	0.00E+00
1.4	2.86E+13	3.72E-04
1.16	2.07E+13	4.60E-04
0.84	4.11E+13	5.30E-04
1.67	1.38E+13	3.47E-04
0.56	3.45E+13	3.24E-04



[methamphetamine]		$k^1 s^{-1}$
[ppm]	[molec/cm <sup>-3</sup> ]	
0	0.00E+00	0
1.4	3.45E+13	9.30E-04
1.16	2.86E+13	6.92E-04
0.84	2.07E+13	5.85E-04
1.67	4.11E+13	1.08E-03
0.56	1.38E+13	4.52E-04

