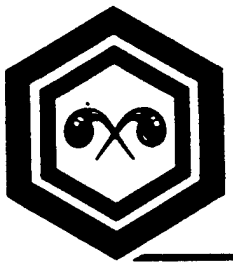

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CHEMICAL REACTIVITY OF LIGHT GASES FOR CATALYTIC AIR PURIFICATION SYSTEMS

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The catalytic oxidation of 11 light gases of direct or potential concern for chemical protection applications was evaluated over a 2% Pt/Al_2O_3 catalyst in a fixed bed catalytic reactor test stand. Each of the 11 light gases was evaluated for reactivity, deactivation potential, and the formation of undesired reaction products. All tests were conducted in a fixed bed catalytic reactor test stand employing 40/60 mesh catalyst particles. The presence of water in the feed stream had a significant effect on the performance of the catalyst. In some cases, the presence of water in the feed stream inhibited the catalytic activity, while in other cases, water enhanced the catalytic activity. Perfluorocyclobutene was the least reactive of the light-gas compounds, requiring the greatest reaction temperture to achieve 99% destruction. Phosgene and cyanogen chloride demonstrated the potential to deactivate the catalyst, but only in dry air. Small amounts of undesired reaction products were observed during oxidation of several of the light gases. However, in most cases, these products were either non-hazardous at their concentration levels, or could be eliminated by increasing the reaction temperature. The oxidation of hydrogen cyanide yielded significant amounts of NO_x, which is difficult to remove from air streams via conventional acid gas scrubbing techniques. Results obtained during this study point to the need to identify catalysts that are capable of destroying perfluorocyclobutene at lower reaction temperatures, stable during the oxidation of phosgene and cyanogen chloride, and able to destroy hydrogen cyanide without the formation of NO_x.

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PREFACE

The work described in this report was authorized under Contract No. DAAA15-91-C-0075. This work was started in November 1993 and completed in January 1995.

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Chemical Reactivity of Light Gases for Catalytic Air Purification Systems

1. INTRODUCTION

Background: Present air purification systems designed for the removal of chemical warfare agents from streams of air are based solely on activated, impregnated carbon, namely ASC whetlerite. Although these filters function well against a wide range of threat compounds, the filters have a limited capacity for agents which are removed by chemical reaction, and those which are weakly adsorbed. Further, the performance of activated carbon filters degrades during prolonged environmental exposure (Rossin et al., 1990). The result of these shortcomings is to place changeout and disposal burdens on applications employing carbon filters. Thus, alternative air purification technologies are being investigated in order to alleviate burdens associated with carbon filtration.

Catalytic oxidation is a candidate technology for the removal of CW agents from air streams. The success of a catalytic air purification system will hinge on the catalyst, which must be able to (1) readily destroy a wide range of dissimilar, heteroatom containing compounds, (2) retain is reactivity for an extended period of time, and (3) not generate toxic by products. The objective of this study is to evaluate the ability of a generic catalyst (Pt/Al_2O_3) to destroy light gases of direct or potential concern to the US Army. A list of compounds evaluated during this effort is reported in Table 1. To meet this objective, the reactivity, stability and product selectivity of the catalyst was evaluated for each compound.

Table 1
Listing of light gases evaluated in this report.

Threat Compound
Perfluoroisobutene
Perfluorocyclobutene
(bis)-Perfluoromethyl disulfide
Trifluoronitrosomethane
Methoxyfluorane
Hydrogen Cyanide
Arsine
Chloropicrin
Cyanogen Chloride
Phosgene
Diphosgene

2. EXPERIMENTAL METHODS

2.1 Materials.

Perfluoroisobutene, perfluorocyclobutene and trifluoronitrosomethane were purchased from PCR Inc. as a compressed gas and used without further purification. (Bis) perfluoromethyl disulfide was obtained from PCR Inc. as a liquid and used without further purification. Chloropicrin was obtained from Aldrich Chemical Co. as a liquid and used without further purification. Methoxyfluorane was obtained from Abbott Hospital Products and used without further purification. 2.2% phosgene in air, 7.5% hydrogen cyanide in helium, and 3.0% arsine in nitrogen were obtained from Matheson as compressed gases. Cyanogen chloride was obtained at Edgewood Arsenal and used without further purification. The 2% $Pt/\alpha\text{-}Al_2O_3$ catalyst employed in this study was obtained from Engelhard as 60/80 mesh granules. The support has a nominal BET surface area of 1-5 m^2/g as reported by the manufacturer. When required, pressure vessels containing different concentrations of each chemical diluted in either air, helium or nitrogen were prepared from the pure material using standard gas handling techniques.

2.2 Catalyst Pretreatment.

The catalyst was pretreated prior to reaction exposure by calcining several 5.0 g catalyst portions in flowing air within a quartz tube furnace. The calcination was performed by raising the temperature to 450°C in one hour under humid air flowing at 500 Nml/min (Nml is defined as one milliliter of gas at 0°C and one atmosphere). The final temperature, 450°C was maintained overnight. The catalyst was then cooled to room temperature with dry air flowing through the catalyst bed. All portions were calcined in this manner and mixed together to obtain the experimental catalyst batch.

2.3 Equipment.

Figure 1 shows a schematic representation of the fixed-bed catalytic reactor system employed in this study. All reactant chemicals, with the exception of methoxyfluorane and chloropicrin, were delivered from individual compressed gas cylinders as compressed gases diluted in either helium, air or nitrogen. Methoxyfluorane and chloropicrin were delivered to the system via a liquid sparger. Although not shown in Figure 1, a Teflon sparger vessel (filled about 60% with liquid chemical) was located within a circulating water bath just after the rotameter. Dry air was metered through the sparger vessel from the reactant mass flow controller bank. PSA dried, oil-free, air was metered to the system using a 0-200 Nml/min mass flow controller. The air stream was delivered to a water saturator, or, if desired, the water saturator could be by-passed such that the test could be conducted in dry air. A back-pressure regulator was located downstream of the water saturator. The water concentration of the feed stream was controlled by controlling the

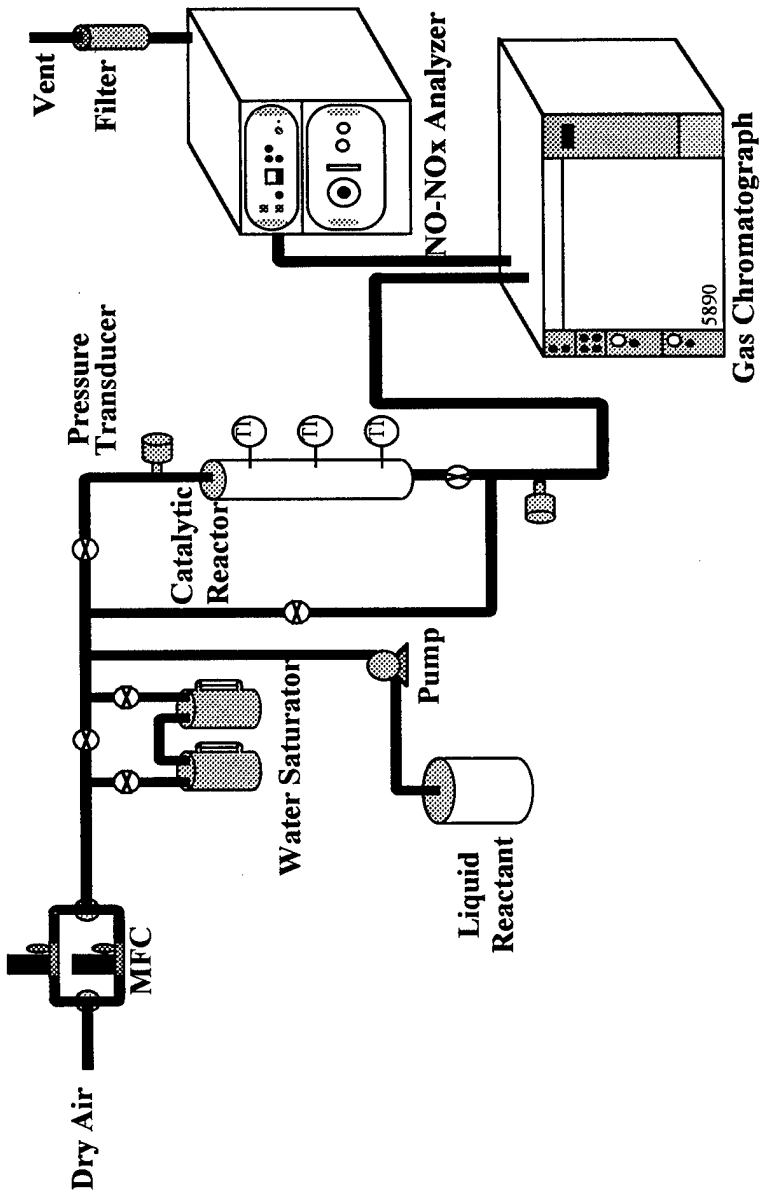


Figure 1: Schematic representation of fixed bed catalytic reactor test stand.

temperature and pressure of the water saturator. The air stream was combined with the reactant stream at a point just up-stream of the catalytic reactor. The reactor was housed in a 7-cm diameter by 20-cm long aluminum block. The aluminum block was employed to insure uniform heating of the catalyst bed. The reactor consisted of a 0.95 cm diameter glass tube. The reactor temperature was controlled by controlling the temperature of the aluminum block. Following the reactor, the effluent was sent to an HP 5890 gas chromatograph (GC) for on-line analysis. Following the GC, the effluent stream was delivered to a filter in order to remove all traces of unreacted chemical. A caustic scrubber was located downstream of the filter in order to remove acid gas reaction products.

The fixed bed reactor consisted of a 0.95 cm o.d. glass tube, approximately 30-cm in length. A schematic representation of the reactor packed with catalyst is illustrated in Figure 2. The catalyst bed was supported on a plug of glass wool located approximately 10 cm from the bottom of the glass reactor tube. The glass wool plug was supported on 12/20 mesh crushed glass held in place using another glass wool plug. The reactor was filled in this manner because HF, a reaction product generated during the oxidation of fluorine-containing compounds, would destroy the first glass wool plug, causing the catalyst bed to drop from the reactor. Approximately 0.2 g of 60/80 mesh crushed glass was placed above the first piece of glass wool to provide a uniform surface for the catalyst bed to rest upon. The catalyst bed was prepared by diluting between 0.25 and 1.25 g of catalyst with 60/80 mesh crushed glass in order to achieve a catalyst bed volume of approximately 2.0 cm^3. The catalyst bed was diluted to minimize axial temperature gradients resulting from the exothermic oxidation reactions. 12/20 mesh crushed glass was placed above the catalyst bed to serve as a pre-heat zone for the incoming feed stream. No thermocouple was placed in the catalyst bed, due to the potential reactivity with the reactant gases. The actual temperature of the catalyst bed could not be monitored. Based on previous work, it was expected that the temperature of the catalyst bed would not deviate more than 1°C from the temperature of the reactor block (Klinghoffer and Rossin, 1992).

2.4 Procedure.

Preparation of Reactant Pressure Vessel: Pressure vessels containing varying concentrations of each chemical were prepared by metering or injecting (depending on whether the reactant was a gas or liquid at room temperature and pressure) a known quantity of pure compound into an evacuated 16.7 liter stainless steel pressure vessel. The vessel was then pressurized to a predetermined pressure (typically between 200 and 400 psig) using dry, ultra-high purity air or suitable diluent. The concentration of each chemical within the pressure vessel was determined using gas chromatographic techniques and referenced to several calibration standards. Calibration standards were prepared by injecting known quantities of pure chemical into one liter gas sampling vessels and drawing gas samples from this mixture for GC analyses.

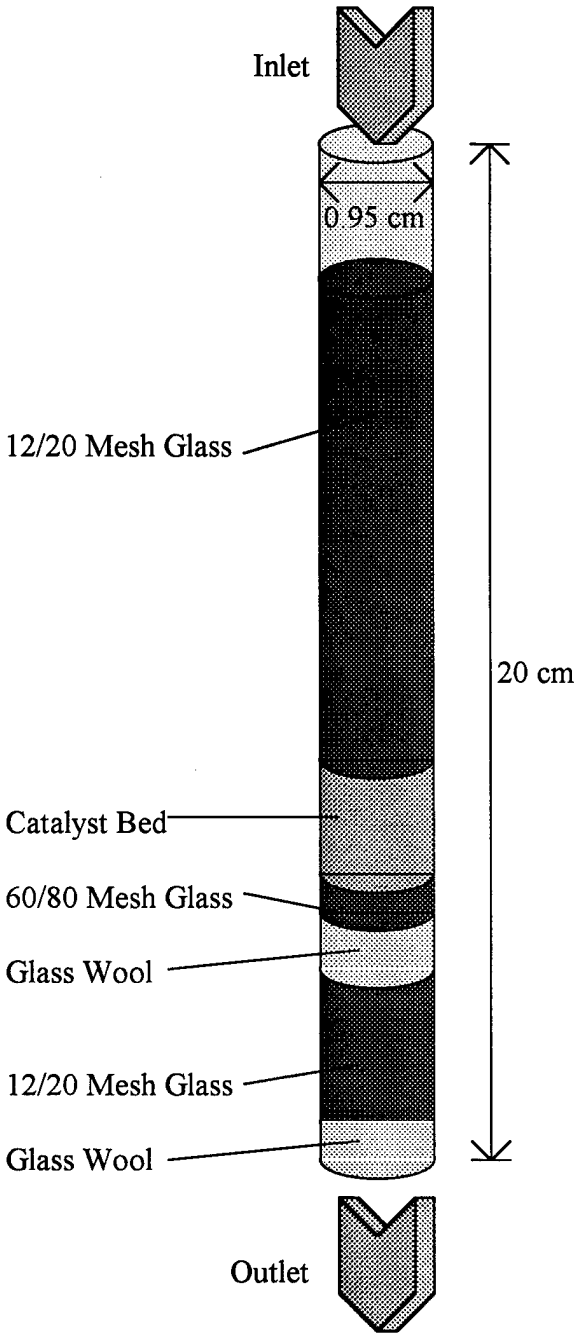


Figure 2: Schematic representation of catalytic reactor.

Performance of Blank Runs: Blank runs were performed in order to assess the thermal stability of each compound. The reactor was filled with 12/20 mesh crushed glass and heated to 400°C overnight. Once at 400°C, the catalyst-free reactor was exposed to 50,000 mg/m^3 of each chemical in dry and humid air at a flow rate of 50 Nml/min. The reactor effluent was sampled every 20 minutes for reactant and CO_2 concentration.

Effects of Water: Approximately 0.75 to 1.20 g of catalyst (60/80 mesh) was diluted with crushed glass (60/80 mesh) to achieve a reactor volume of 2.0 cm^3. The catalyst/diluent mixture was then loaded into the reactor and heated from room temperature to 400-500°C (depending on the compound) overnight in flowing dry air. Once at reaction temperature, the catalyst was exposed to 50,000 mg/m^3 of each chemical in dry air at a residence time (referenced to 0°C and one atmosphere) of 0.8 sec. The initial temperature was maintained for one hour, after which, the catalyst bed temperature was decreased at a rate of 30°C/hr. The effluent was sampled for the concentration of each chemical and CO_2 every 20 minutes (10°C temperature intervals). Once the conversion of reactant was below 10%, the reactant flow was discontinued and the reactor was returned to the initial reaction temperature overnight. The experiment was then repeated the following morning in humid air (3.0% water).

Catalyst Stability: Long term stability testing was performed only for phosgene and cyanogen chloride. This is because results obtained during reactivity analyses indicated that the catalyst was deactivating. Approximately 0.4 to 1.0 grams of catalyst (60/80 mesh) was diluted with crushed glass (60/80 mesh) to achieve a reactor volume of 2.0 cm^3. The catalyst/diluent mixture was then loaded into the reactor and heated from room temperature to 400-450°C (depending on the compound) overnight in flowing dry air. Once at reaction temperature, the catalyst was exposed to 10,000 and 45,800 mg/m^3, respectively, of phosgene and cyanogen chloride in dry air at residence times of 0.3 and 0.8 sec., respectively. The effluent was sampled for the concentration of reactant chemical and CO_2 every 20 minutes, and the catalyst was kept on-line for approximately five hours in each experiment.

Effluent Analysis: Reactor effluent was analyzed on-line using a Hewlett-Packard 5890 series II gas chromatograph equipped with a flame ionization detector (FID) and a thermal conductivity detector (TCD). Permanent gases were separated using a 2-m by 3.2-mm 60/80 mesh Hayesep Q column and analyzed using the TCD. The concentration of the reactant chemical was determined using either a 3-m by 3.2-mm 5% Krytox 14B on 60/80 mesh Graphpac GB, or a 2.7 m by 3.2 mm 10% SP-2401 on 80/100 mesh Supelcoport in conjunction typically with the FID (phosgene was analyzed using the TCD). The Krytox column was used to separate perfluoroisobutene, perfluorocyclobutene, perfluoromethyl disulfide, trifluoronitrosomethane, halothane, hydrogen cyanide, arsine, cyanogen chloride and phosgene. The Supelcoport column was used to separate methoxyfluorane and chloropicrin. A Hewlett-Packard 5971 mass spectrometer was used to identify any unknown compounds in the reactor effluent.

3. RESULTS

Each reactant chemical was evaluated for relative reactivity and formation of reaction products. Based on reactivity results, selected chemicals were used to evaluate the stability of the catalyst. In evaluating the reactivity of each compound, an initial test was performed aimed at evaluating the effects of water on catalytic activity. If water was found to have a significant effect on catalytic activity, future tests would be conducted over conditions where the catalyst displayed the least activity. For the fluorine-containing compounds, the relative reactivity was assessed by challenging the catalyst with 16,700 and 50,000 mg/m^3 of chemical at 350 and 400°C, and varying the residence time until the conversion of the reactant chemical exceeded 99%. The compound from this group which required the greatest residence time to achieve the 99% conversion level was declared the least reactive.

For the representative of blood and choking agents, time did not allow for recording conversion-residence time data similar to that recorded for the fluorine-containing compounds. Only conversion-temperature data were recorded for these compounds. As a result, the least reactive compound was declared to be the compound which required the greatest temperature to achieve greater than 99% conversion.

3.1 Oxidation of Perfluorocyclobutene.

Blank Run: A blank run was performed to determine the thermal stability of perfluorocyclobutene. Data were recorded at 400°C employing a feed concentration of 6,900 ppm (50,000 mg/m^3) in dry air flowing at 50 Nml/min. No significant conversion was observed (to within experimental error) over a two hour period, indicating that the compound was thermally stable at reaction conditions.

Effects of Water: The effect of water on the conversion of 50,000 mg/m^3 (6,900 ppm) perfluorocyclobutene as a function of reaction temperature in dry ($T_{dew} \leq$-40°C; 0.02 %) and humid (T_{dew} = 29°C, 4.0 %) air is reported in Figure 3. Data reported in this figure correspond to a residence time of 0.8 seconds. The dew point temperature of <-40°C corresponds to dry air delivered from a PSA drier. These dew point temperatures were chosen to correspond to the minimum and maximum dew point temperatures expected in an outdoor environment. Results presented in this figure demonstrate that the presence of water has a significant inhibition effect on the catalytic activity. For example, at 400°C, the conversion of perfluorocyclobutene in dry air is 72%, while that in humid air is only 18%. Results suggest that the concentration of water has a significant impact on the performance of the catalyst, and therefore warrants further studies. Based on results presented in this figure, all subsequent experiments with perfluorocyclobutene were conducted in humid air.

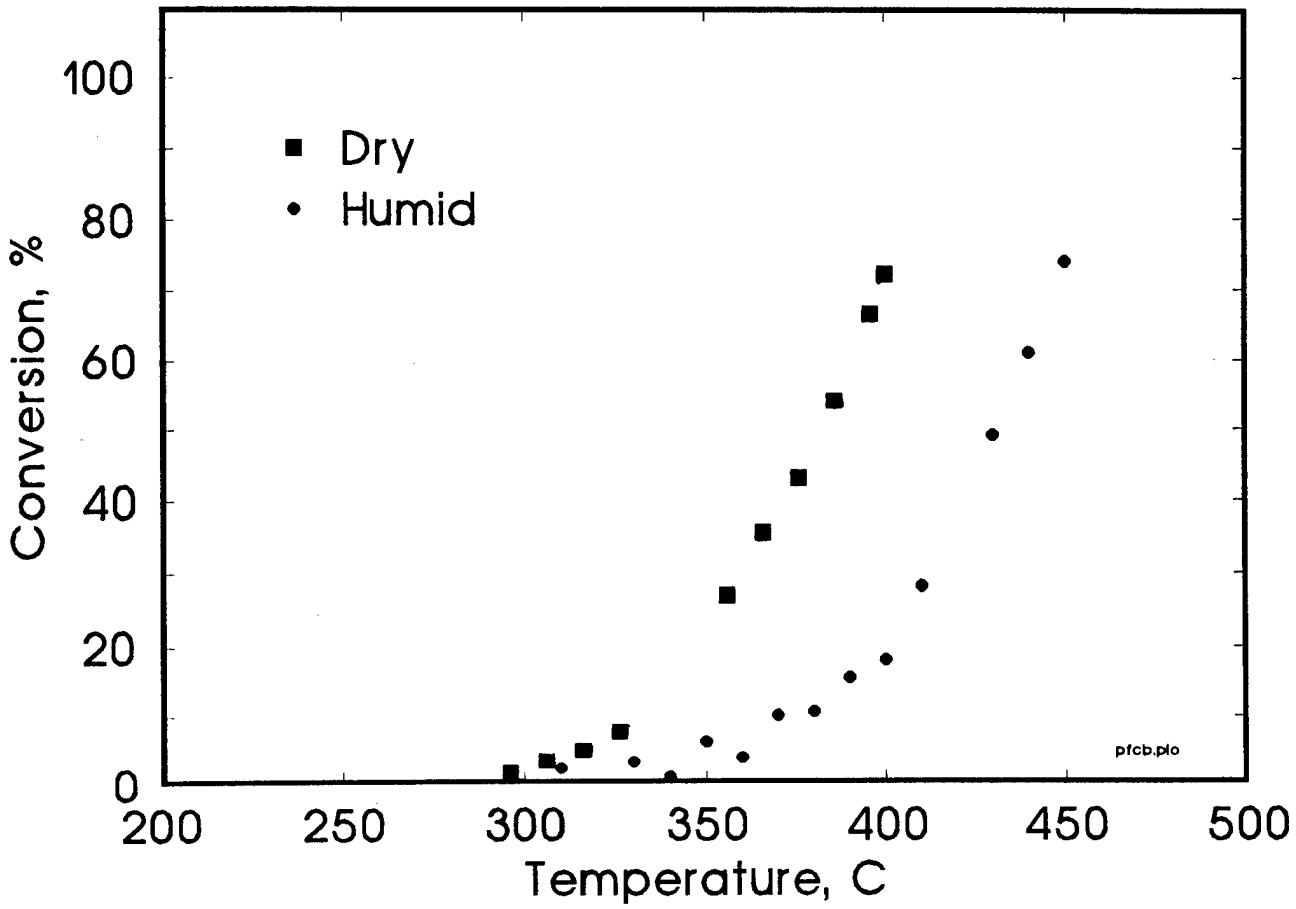


Figure 3: Conversion as a function of reaction temperature for the oxidation of 50,000 mg/m^3 perfluorocyclobutene in dry and humid air. Residence time = 0.80 s.

Effects of Residence Time: Figure 4 presents a plot of reduction ratio (C_{eff}/C_{feed}) as a function of residence time for the oxidation of 16,700 and 50,000 mg/m^3 (2,300 and 6,900 ppm) perfluorocyclobutene at 400°C in humid (T_{dew} = 29°C, 4 % H_2O) air. The solid line present in the figure represent the 99% conversion level. Results presented in this figure indicate that a residence time on the order of 8 seconds is required to achieve 99% destruction of perfluorocyclobutene over the 2% Pt/α-Al_2O_3 catalyst. Note also from this figure that decreasing the feed concentration by a factor of three did not affect the conversion, indicating that the oxidation of perfluorocyclobutene proceeds via first order kinetics over the catalyst.

Table 2 summarizes the results for the oxidation of perfluorocyclobutene at 400°C.

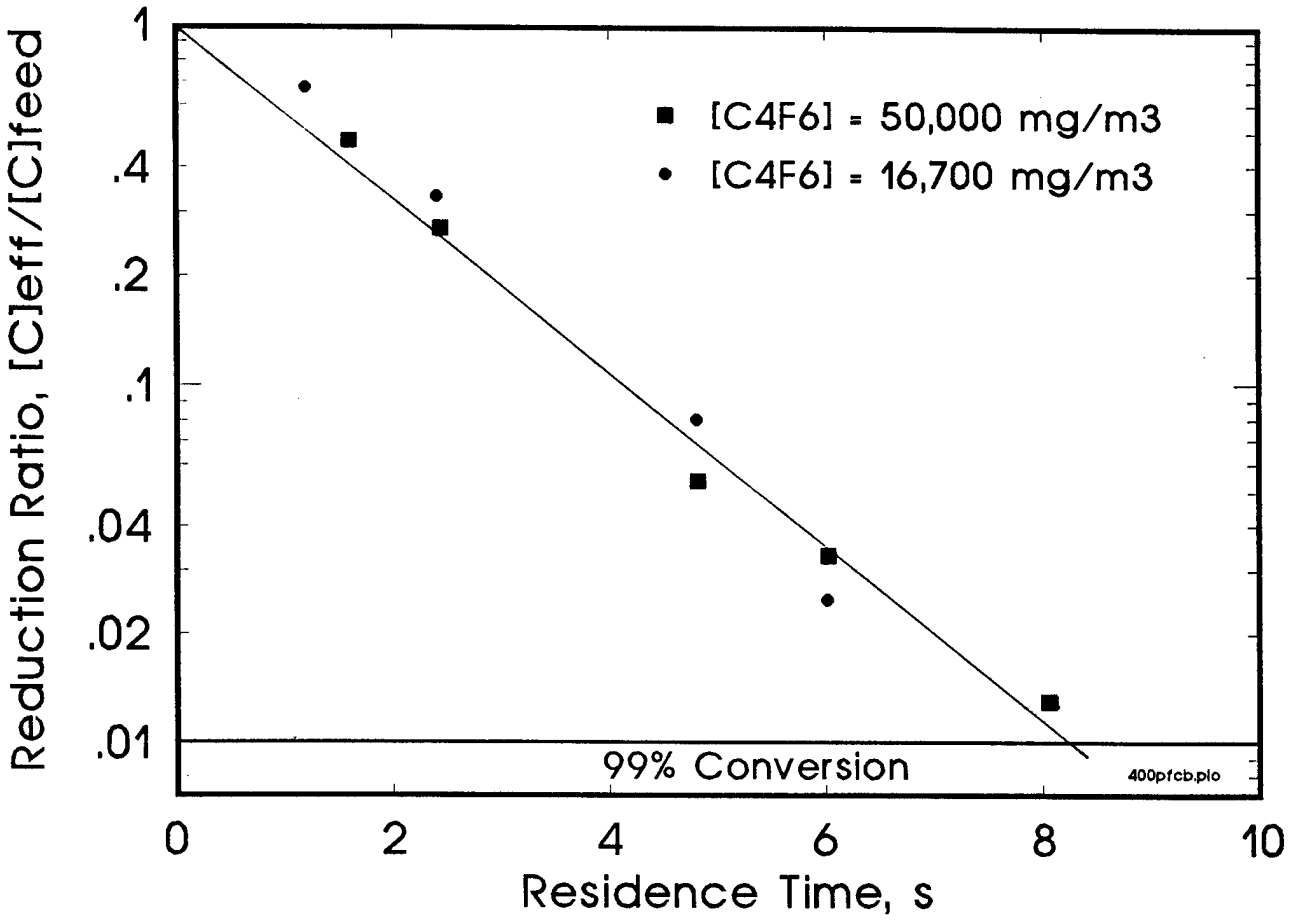


Figure 4: Perfluorocyclobutene reduction ratio as a function of residence time at 400°C.

Table 2
Run Summary for the Oxidation of Perfluorocyclobutene at 400°C

Run	Feed [C]	Conversion	Res. Time
3/25a/93	50,000 mg/m^3	52.41%	1.6 s
3/25b/93	50,000 mg/m^3	72.59%	2.4 s
3/25c/93	50,000 mg/m^3	94.61%	4.8 s
3/25d/93	50,000 mg/m^3	96.69%	6.0 s
3/26a/93	50,000 mg/m^3	98.70%	8.0 s
3/29a/93	16,700 mg/m^3	32.86%	1.2 s
3/30a/93	16,700 mg/m^3	66.86%	2.4 s
3/30b/93	16,700 mg/m^3	91.98%	4.8 s
3/30c/93	16,700 mg/m^3	97.50%	6.0 s

Reaction Products: The only reaction product identified via on-line GC analysis was CO_2. No CO nor products of partial oxidation were observed when conducting the tests in humid air. Carbon balances were typically 100±5%, indicating that the concentration of COF_2, or other products of incomplete oxidation, if formed, would be small. The major

fluorine-containing reaction product is suspected to be HF, due to the etching of the glass reactor and crushed glass located down-stream of the catalyst bed.

3.2 Oxidation of (bis) Perfluoromethyl Disulfide.

Blank Run: A blank run was performed to determine the thermally stability of (bis) perfluoromethyl disulfide. Data were recorded at 400°C employing a feed concentration of 50,000 mg/m^3 (5,550 ppm) in dry air flowing at 50 Nml/min. The conversion of this compound was approximately 50% at these conditions, indicating that (bis) perfluoromethyl disulfide is not thermally stable under these conditions.

Effects of Water: The effect of water on the conversion of 50,000 mg/m^3 (bis) perfluoromethyl disulfide as a function of reaction temperature in dry (T_{dew} ≤-40°C; 0.02%) and humid (T_{dew} = 29°C; 4.0 %) air is reported in Figure 5. Data presented in this figure correspond to a residence time of 0.8 seconds. Results presented in this figure indicate that the presence of water, to within experimental error, does not have an effect on the catalytic activity.

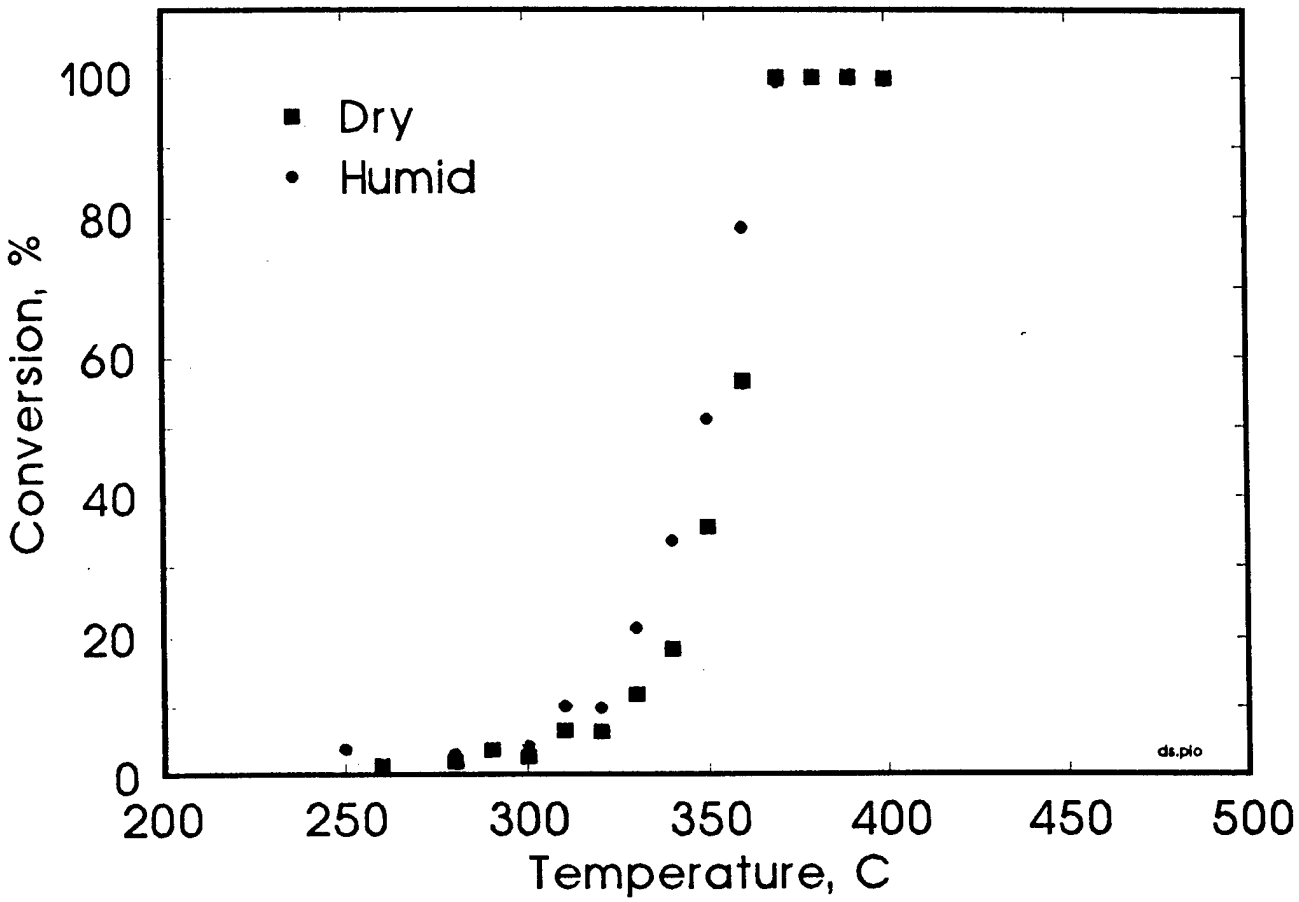


Figure 5: Conversion as a function of reaction temperature for the oxidation of 50,000 mg/m^3 (bis) perfluoromethyl disulfide in dry and humid air. Residence time = 0.80 s.

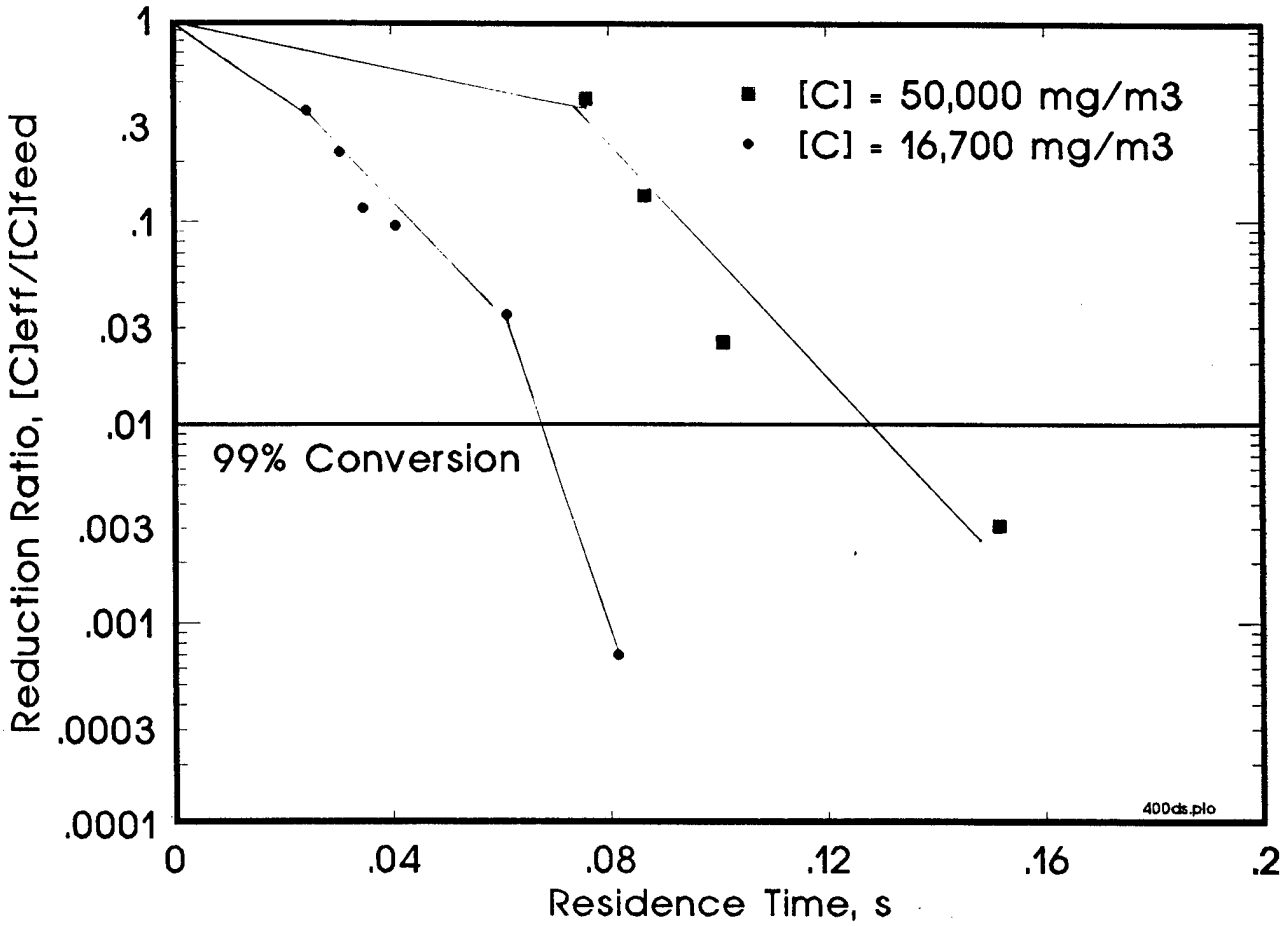


Figure 6: (Bis) perfluoromethyl disulfide reduction ratio as a function of residence time at 400°C.

Effect of Residence Time: Figure 6 presents a plot of the reduction ratio (C_{eff}/C_{feed}) as a function of residence time for the oxidation of 16,700 and 50,000 mg/m^3 (1,850 and 5,550 ppm) (bis) perfluoromethyl disulfide in humid (T_{dew} = 29°C; 4.0 %) air at 400°C. Similar data recorded at 350°C are reported in Figure 7. At 400°C, residence times of approximately 0.07 and 0.13 seconds are required to achieve the 99% conversion level for feed concentrations of 16,700 and 50,000 mg/m^3, respectively. Decreasing the reaction temperature to 350°C increased the 99% conversion residence time to approximately 0.25 and 2.5 seconds, respectively, for feed concentrations of 16,700 and 50,000 mg/m^3. Decreasing the feed concentration by a factor of three significantly decreased the required residence time at both temperatures. Results presented in Figures 6 and 7 results indicate that the oxidation of (bis) perfluoromethyl disulfide is strongly dependent on reaction temperature and feed concentration.

During tests conducted with (bis) perfluoromethyl disulfide, the catalytic activity increased with time-on-stream. This result was similar to that observed by Rossin[3] during a study involving the oxidation of diethyl sulfide over a platinum alumina catalyst. Because of this behavior, the catalyst bed was replaced after a few hours of service. Tables 3 and 4 summarize results obtained for the oxidation of (bis) perfluoromethyl disulfide at 350 and 400°C.

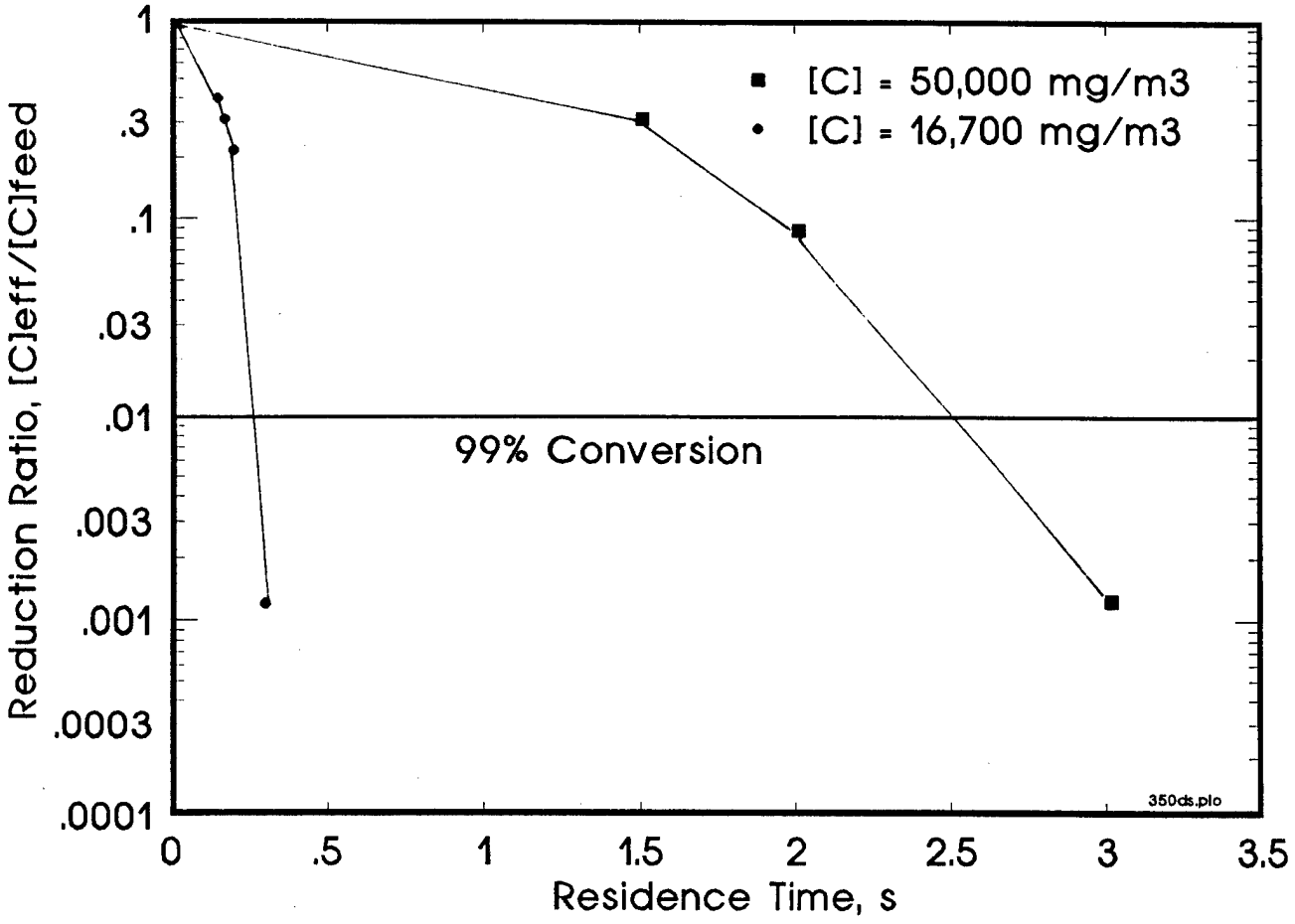


Figure 7: (Bis) perfluoromethyl disulfide reduction ratio as a function of residence time at 350°C.

Table 3
Run Summary for the Oxidation of (bis) perfluoromethyl disulfide at 350°C

Run	Feed [C]	Conv	τ
6/21a/93	50,000 mg/m^3	99.88%	3.00 s
6/21b/93	50,000 mg/m^3	68.72%	1.50 s
6/21c/93	50,000 mg/m^3	91.28%	2.00 s
6/23a/93	16,700 mg/m^3	99.89%	0.30 s
6/23b/93	16,700 mg/m^3	61.12%	0.15 s
6/23c/93	16,700 mg/m^3	78.36%	0.20 s
6/23d/93	16,700 mg/m^3	68.95%	0.17 s

Table 4
Run Summary for the Oxidation of (bis) perfluoromethyl disulfide at 400°C

Run	Feed [C]	Conv	τ
6/8a/93	50,000 mg/m^3	58.05%	0.076 s
6/8b/93	50,000 mg/m^3	86.42%	0.087 s
6/4a/93	50,000 mg/m^3	97.46%	0.101 s
6/4b/93	50,000 mg/m^3	99.69%	0.152 s
6/11a/93	16,700 mg/m^3	77.47%	0.031 s
6/11b/93	16,700 mg/m^3	88.26%	0.035 s
6/11c/93	16,700 mg/m^3	90.47%	0.041 s
6/11d/93	16,700 mg/m^3	63.70%	0.025 s
6/14a/93	16,700 mg/m^3	99.93%	0.082 s
6/14b/93	16,700 mg/m^3	96.55%	0.061 s

Reaction Products: The only reaction products identified via on-line GC analysis were CO_2 and SO_2. No additional carbon- or sulfur-containing reaction products were observed. Carbon balances were typically 100±5% for all runs. No fluorine-containing reaction products were identified. However, based on the etching the glass reactor tube, it is suspected that significant quantities of HF were generated during the oxidation of (bis) perfluoromethyl disulfide.

3.3 Oxidation of Perfluoroisobutene.

Blank Run: A blank run was performed to determine the thermal stability of perfluoroisobutene. Data were recorded at 400°C employing a feed concentration of 50,000 mg/m^3 (5,700 ppm) in dry air flowing at 50 Nml/min. No significant conversion was observed (to within experimental error) over a two hour period, indicating that the compound was thermally stable at reaction conditions.

Effects of Water: The effect of water on the conversion of 50,000 mg/m^3 perfluoroisobutene as a function of reaction temperature in dry ($T_{dew} \leq$-40°C; 0.02%) and humid (T_{dew} = 29°C; 4.0 %) air is reported in Figure 8. Data presented in this figure correspond to a residence time of 0.8 seconds. Results presented in this figure indicate that the addition of water to the feed inhibits the oxidation of perfluoroisobutene. Because of this behavior, all future tests with perfluoroisobutene were performed in humid air.

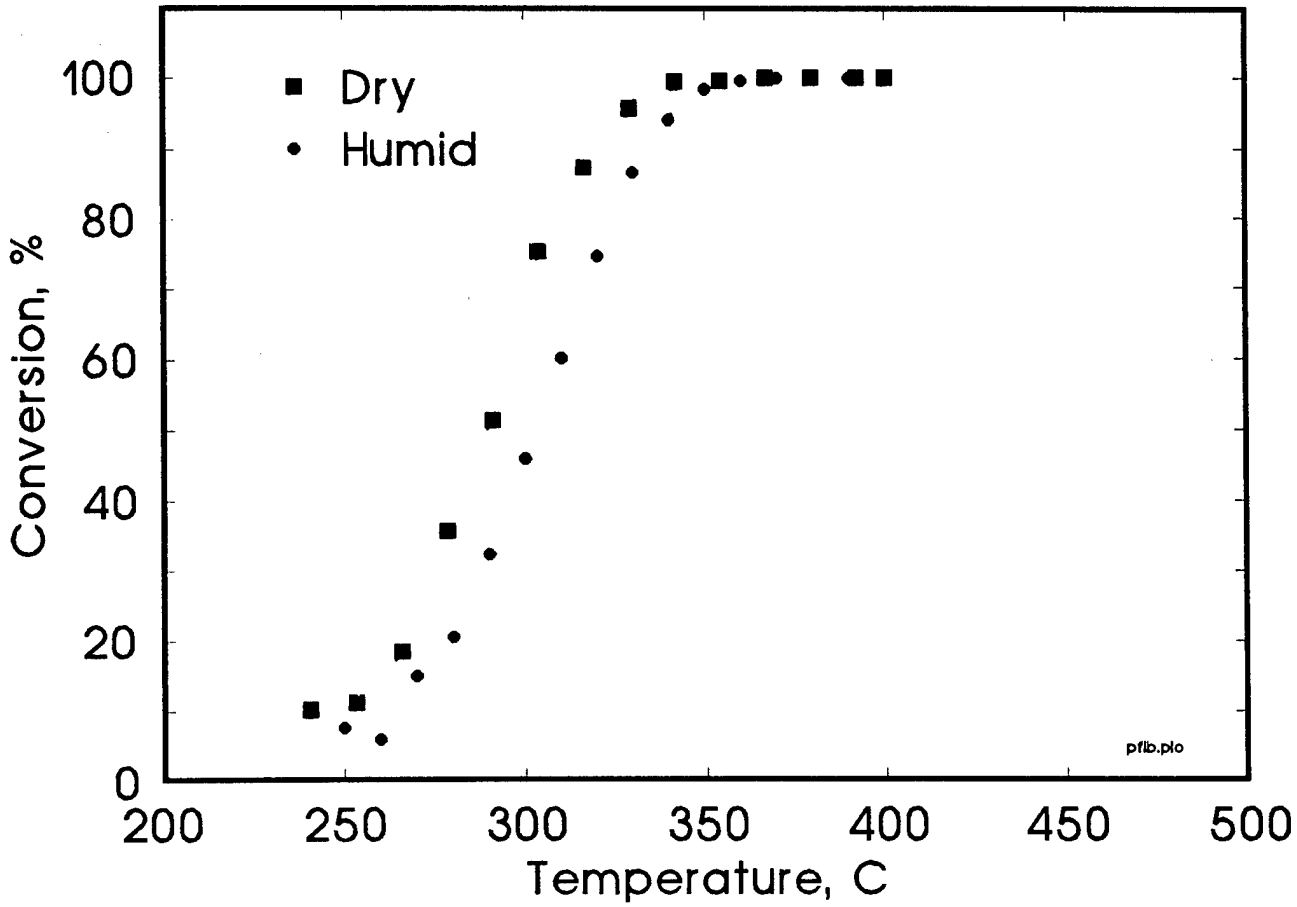


Figure 8: Conversion as a function of reaction temperature for the oxidation of 50,000 mg/m^3 perfluoroisobutene in dry and humid air. Residence time = 0.80 s.

Effect of Residence Time: Figure 9 presents a plot of the reduction ratio (C_{eff}/C_{feed}) as a function of residence time for the oxidation of 16,700 and 50,000 mg/m^3 (1,900 and 5,700 ppm) perfluoroisobutene in humid (T_{dew} = 29°C; 4.0 %) air at 350°C. Similar data recorded at 400°C are reported in Figure 10. Feed concentration did not have an effect on the conversion of perfluoroisobutene, to within experimental error, indicating that the oxidation of perfluoroisobutene proceeds according to first order kinetics. At 400°C, a residence time of approximately 0.4 seconds is required to achieve 99% destruction. Decreasing the reaction temperature to 350°C increases the required residence time to 1.0 seconds. Tables 5 and 6 summarize results obtained for the oxidation of perfluoroisobutene at 350 and 400°C.

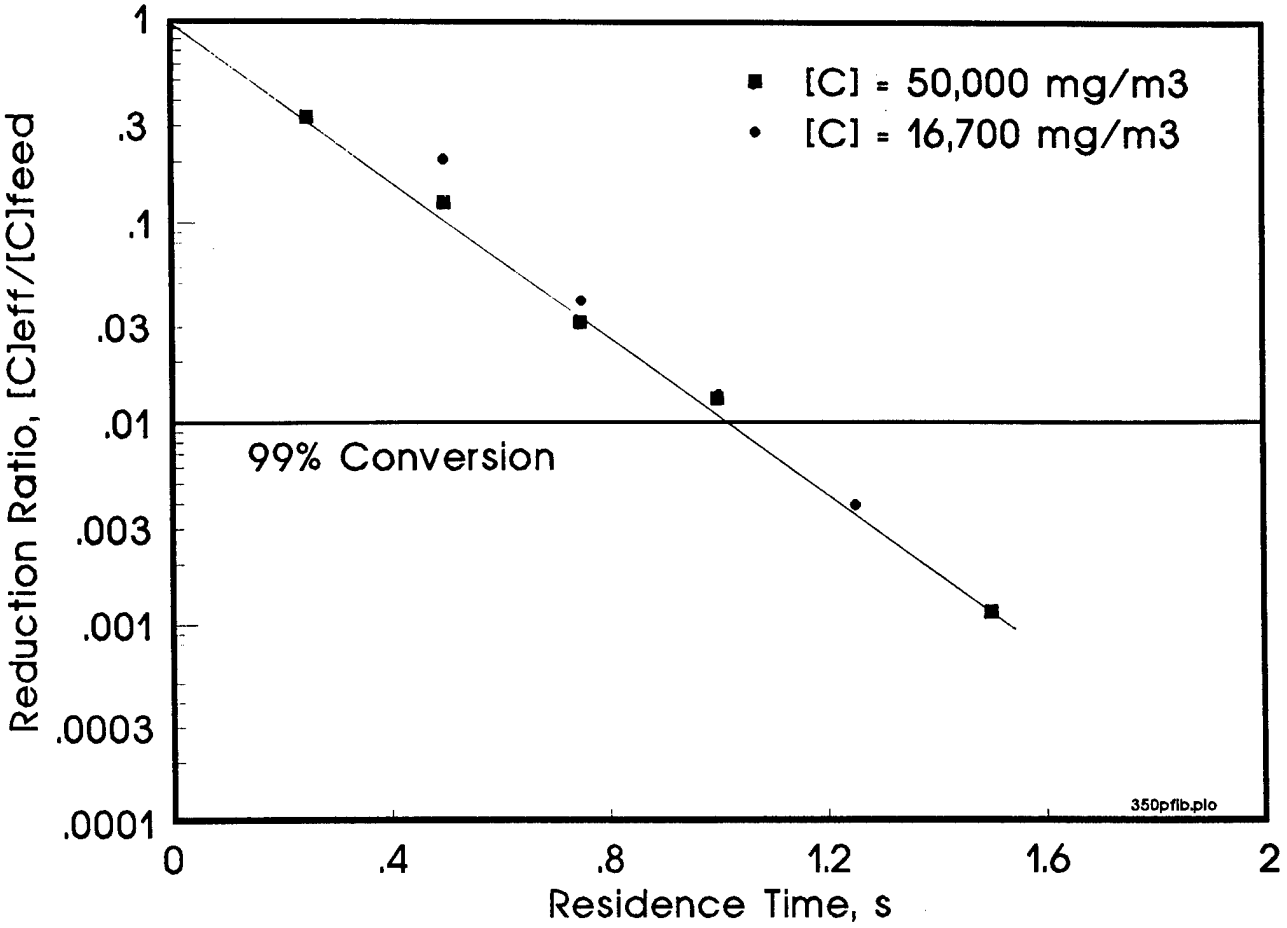


Figure 9: Perfluoroisobutene reduction ratio as a function of residence time at 350°C.

Table 5
Run Summary for the Oxidation of Perfluoroisobutene at 350°C

Run	Feed [C]	Conv	τ
7/15a/93	50,000 mg/m^3	96.86%	0.75 s
7/15b/93	50,000 mg/m^3	99.88%	1.50 s
7/15c/93	50,000 mg/m^3	98.70%	1.00 s
7/15d/93	50,000 mg/m^3	87.32%	0.50 s
7/15e/93	50,000 mg/m^3	66.95%	0.25 s
7/16a/93	50,000 mg/m^3	79.44%	0.50 s
7/19a/93	16,700 mg/m^3	95.94%	0.75 s
7/19b/93	16,700 mg/m^3	98.63%	1.00 s
7/19d/93	16,700 mg/m^3	99.61%	1.25 s

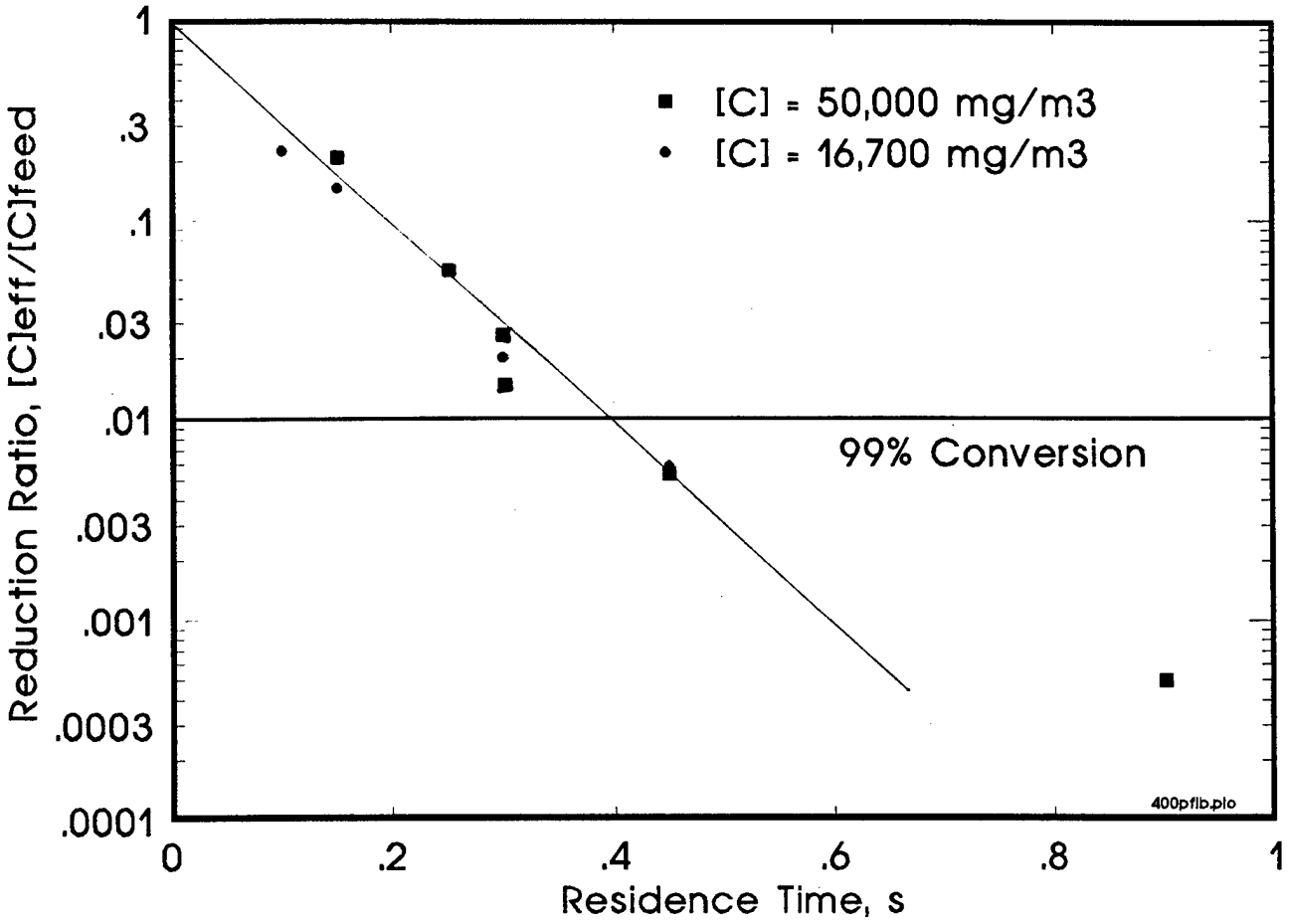


Figure 10: Perfluoroisobutene reduction ratio as a function of residence time at 400°C.

Table 6
Run Summary for the Oxidation of Perfluoroisobutene at 400°C

Run	Feed [C]	Conv	τ
7/13a/93	50,000 mg/m^3	69.00%	0.10 s
7/13b/93	50,000 mg/m^3	48.81%	0.05 s
7/13c/93	50,000 mg/m^3	94.41%	0.25 s
7/13d/93	50,000 mg/m^3	79.33%	0.15 s
7/14c/93	50,000 mg/m^3	97.41%	0.30 s
7/14d/93	50,000 mg/m^3	99.47%	0.45 s
7/14e/93	50,000 mg/m^3	99.95%	0.90 s
7/12a/93	50,000 mg/m^3	98.54%	0.30 s
7/13e/93	16,700 mg/m^3	77.47%	0.10 s
7/13f/93	16,700 mg/m^3	85.25%	0.15 s
7/14a/93	16,700 mg/m^3	98.00%	0.30 s
7/14b/93	16,700 mg/m^3	99.42%	0.45 s

Reaction Products: The only reaction product identified via on-line GC analysis was CO_2. No CO nor products of partial oxidation were observed when conducting the tests in humid air. Carbon balances were typically 100±5%, indicating that significant quantities of COF_2 were not formed. The major fluorine containing reaction product is suspected to be HF, due to the etching of the glass reactor and crushed glass located down-stream of the catalyst bed.

3.5 Oxidation of Perfluoronitrosomethane.

Blank Run: A blank run was performed to determine the thermal stability of perfluoronitrosomethane. Data were recorded at 400°C employing a feed concentration of 50,000 mg/m^3 (11,300 ppm) in dry air flowing at 50 Nml/min. Under these test conditions, the conversion of perfluoronitrosomethane was 99.8%, indicating that the compound is not thermally stable. The presence of near stoichiometric quantities of CO_2 in the effluent stream confirmed the fact that chemical reaction was occurring. Increasing the flow rate (constant perfluoronitrosomethane concentration) from 50 to 100 to 200 Nml/min did not have a significant effect on conversion, as the conversion remained constant at approximately 99.8% during these tests. Tests were then repeated at 350, 300 and 250°C for a flow rate of 50 Nml/min. During these tests, the conversion of perfluoronitrosomethane decreased from 99.8 to 99.0 to 30.0%. These results indicate that perfluoronitrosomethane is not thermally stable at reaction temperatures above about 250°C.

Effect of Water: The effect of water on the conversion of 50,000 mg/m^3 perfluoronitrosomethane as a function of reaction temperature in dry (T_{dew} ≤-40°C; 0.02%) and humid (T_{dew} = 29°C; 4.0 %) air is reported in Figure 11. Data presented in this figure correspond to a residence time of 0.8 seconds. Results presented in this figure indicate that the addition of water to the feed inhibits the oxidation of perfluoronitrosomethane.

Reaction Products: During the above experiments, an unknown reaction product was observed via gas chromatographic analysis. The reaction product was subsequently identified as perfluoronitromethane (CF_3NO_2) using GC/MS techniques. Figure 12 shows a plot of the selectivity towards the formation of this product as a function of temperature during the oxidation of perfluoronitrosomethane in humid air. The selectivity towards formation of this product decreases from 20 to about 15% as the reaction temperature is increased from 330 to 430°C. Evidently, this product was formed by the partial oxidation of perfluoronitrosomethane. Mass spectral data for perfluoronitromethane and perfluoronitrosomethane are reported in Figure 13.

Effect of Residence Time: Because of the high reactivity of perfluoronitrosomethane (Figure 11), residence time studies were not conducted.

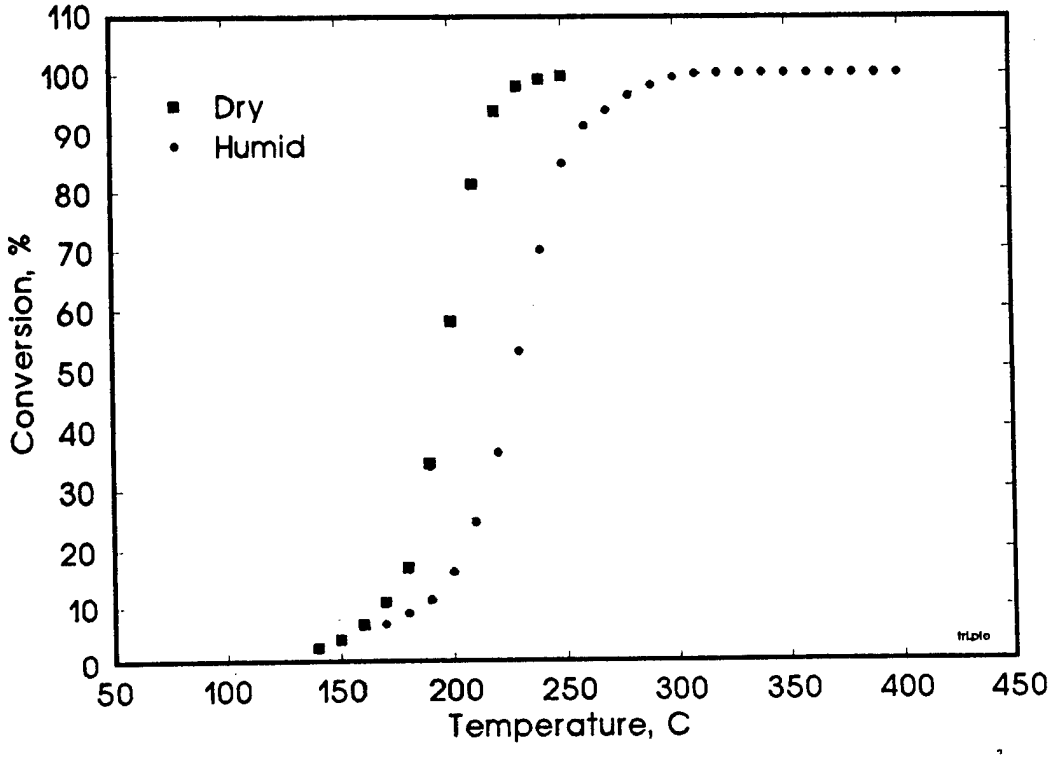


Figure 11: Conversion as a function of reaction temperature for the oxidation of 50,000 mg/m^3 perfluoronitrosomethane in dry and humid air. Residence time = 0.80 s.

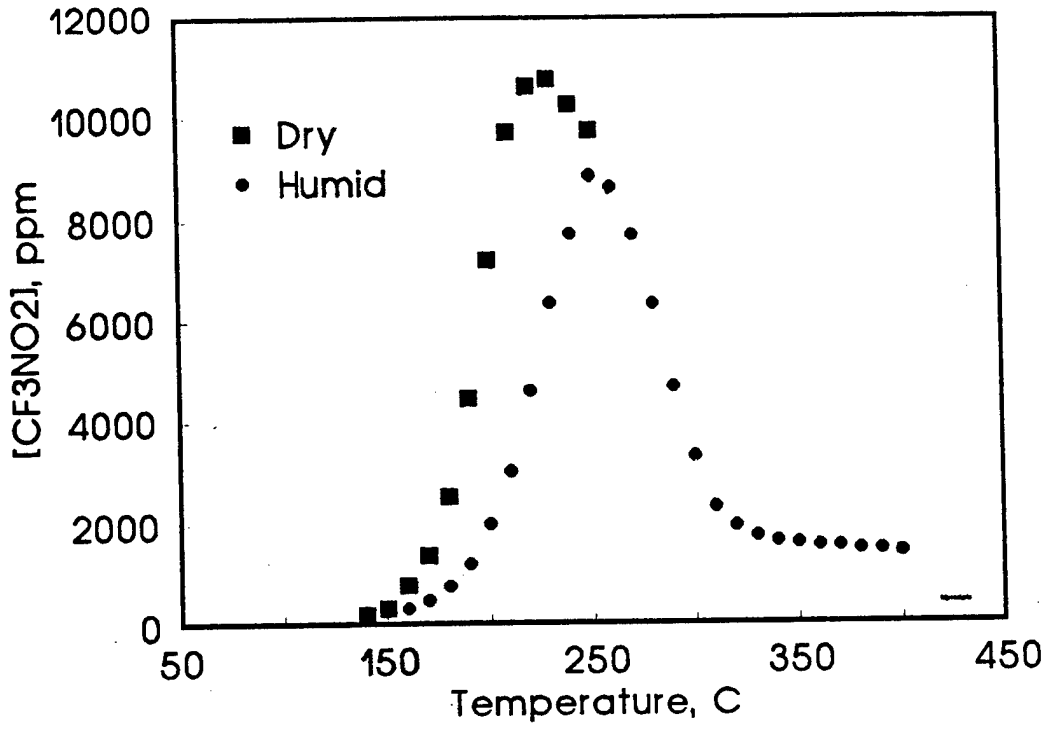


Figure 12: Concentration of perfluoro*nitro*methane (CF_3NO_2) as a function of temperature during the oxidation of perfluoro*nitroso*methane (CF_3NO) in dry and humid air.

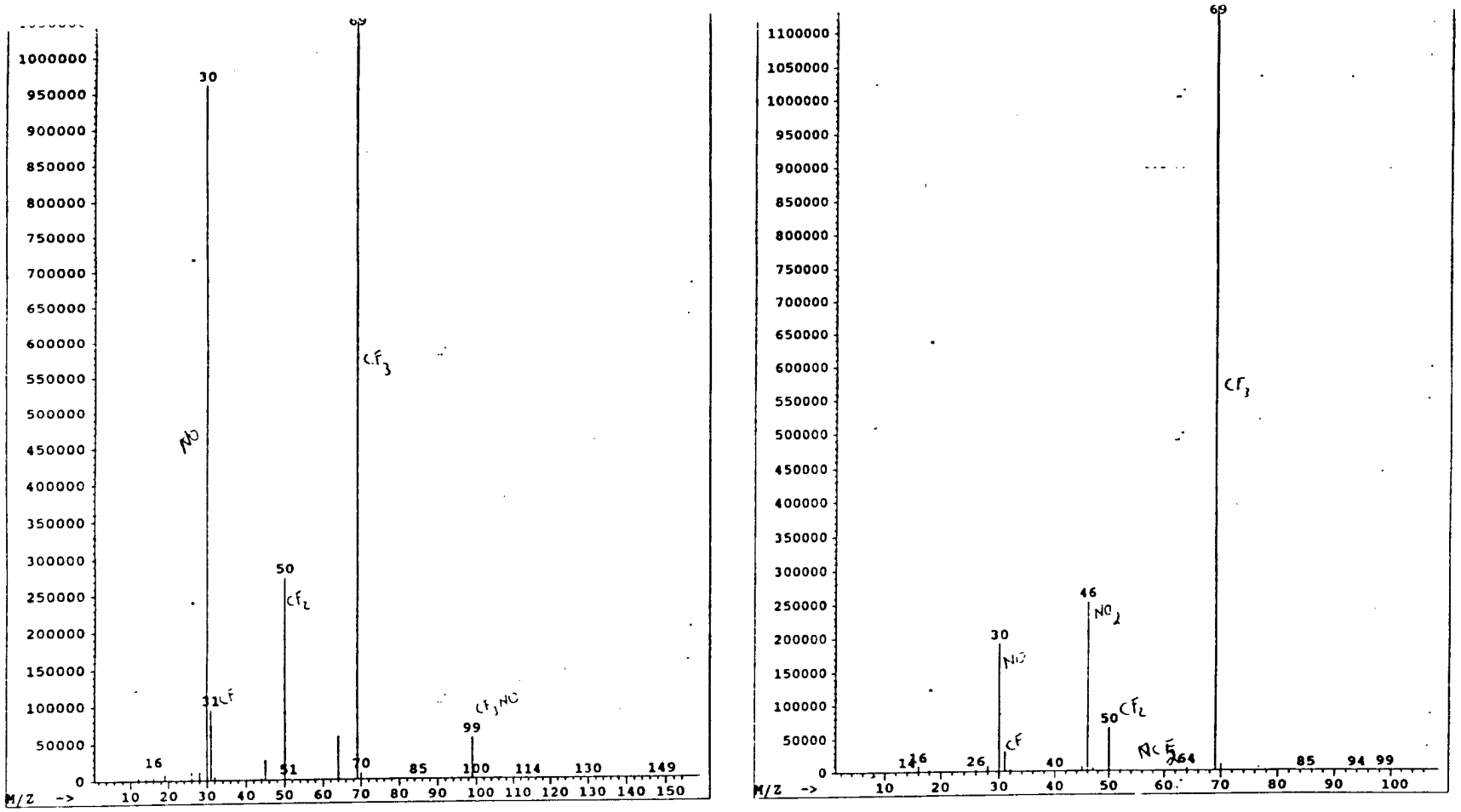


Figure 13: Mass spectral data for (A) perfluoro*nitroso*methane and (B) perfluoro*nitro*methane.

3.5 Oxidation of Methoxyfluorane.

Blank Run: A blank run was performed to determine the thermal stability of methoxyfluorane. Data were recorded for reaction temperatures between 450°C to 300°C employing a feed concentration of 50,000 mg/m^3 (6,800 ppm) at a flow rate of 50 Nml/min. The reaction was conducted in dry air and at atmospheric pressure. At 450°C, the conversion of methoxyfluorane was 35%, indicating that the compound is somewhat unstable at this temperature. For reaction temperatures below 400°C, the conversion decreased to less than 15%.

Effect of Water: The effect of water on the conversion of 50,000 mg/m^3 methoxyfluorane as a function of reaction temperature in dry ($T_{dew} \leq$-40°C; 0.02 %) and humid (T_{dew} = 29 °C, 4.0 %) air is reported in Figure 14. Data reported in this figure correspond to a residence time of 0.8 seconds. Results presented in this figure show that the compound is highly reactive. At 300°C, the conversion of methoxyfluorane is greater than 99.9% whether the run was conducted in dry or humid air.

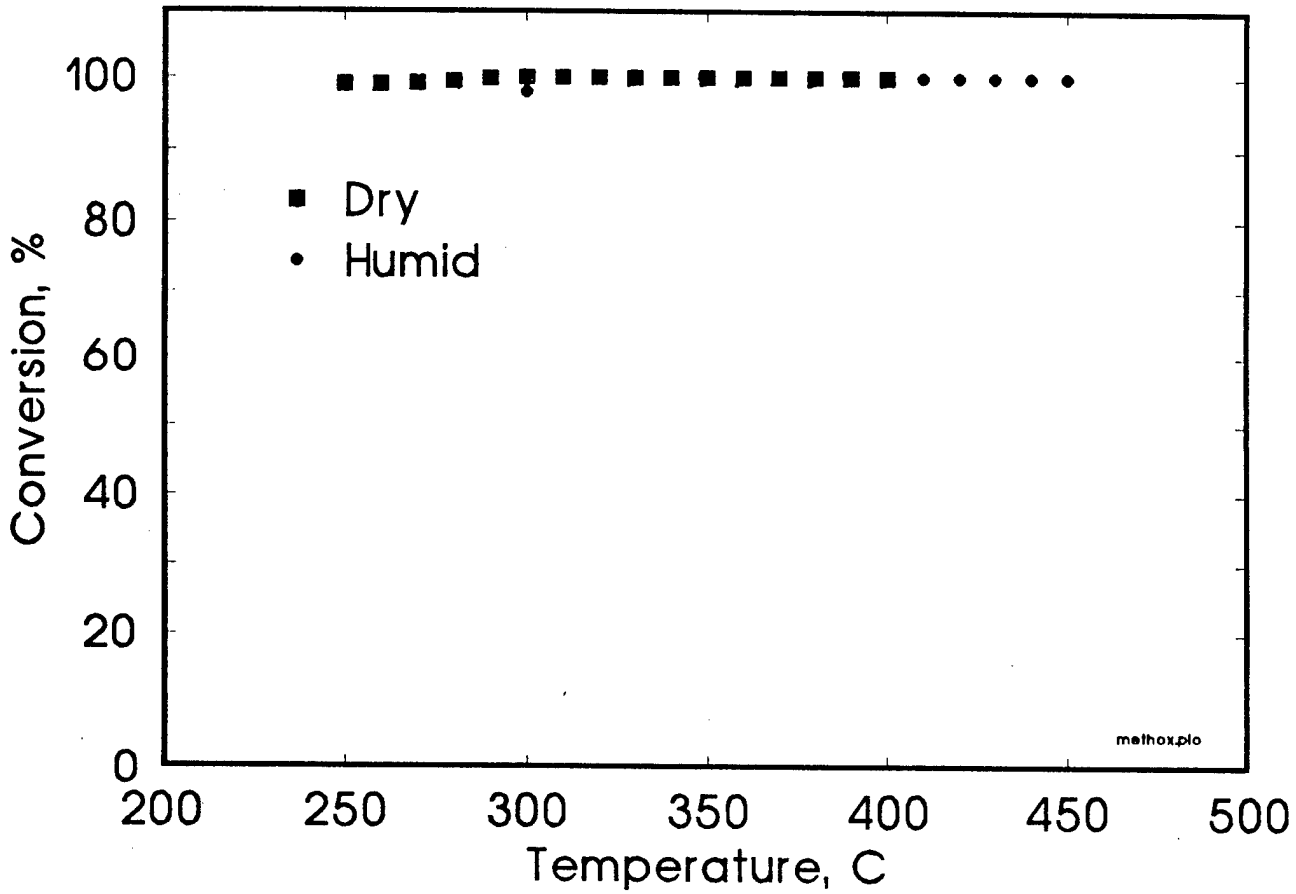


Figure 14: Conversion as a function of reaction temperature for the oxidation of 50,000 mg/m^3 methoxyfluorane in dry and humid air. Residence time = 0.80 s.

Reaction Products: Reaction products consisted of CO_2 and HF. HF is suspected due to the clouding of the glass reactor tube. Eight unidentified (estimated maximum concentration 100 ppm) reaction products were observed during FID analysis of the reactor effluent. Malfunctions in the mass selective detector during testing of this compound prevented identification.

Effect of Residence Time: Because of the high reactivity of this compound, residence time studies were not conducted.

3.6 Oxidation of Phosgene.

Blank Run: A blank run was conducted to assess the thermal stability of phosgene. Data were recorded at 400°C employing a phosgene feed concentration of 11,300 ppm (50,000 mg/m^3) in dry air flowing at 50 Nml/min. No significant conversion of phosgene was observed over a two hour time period.

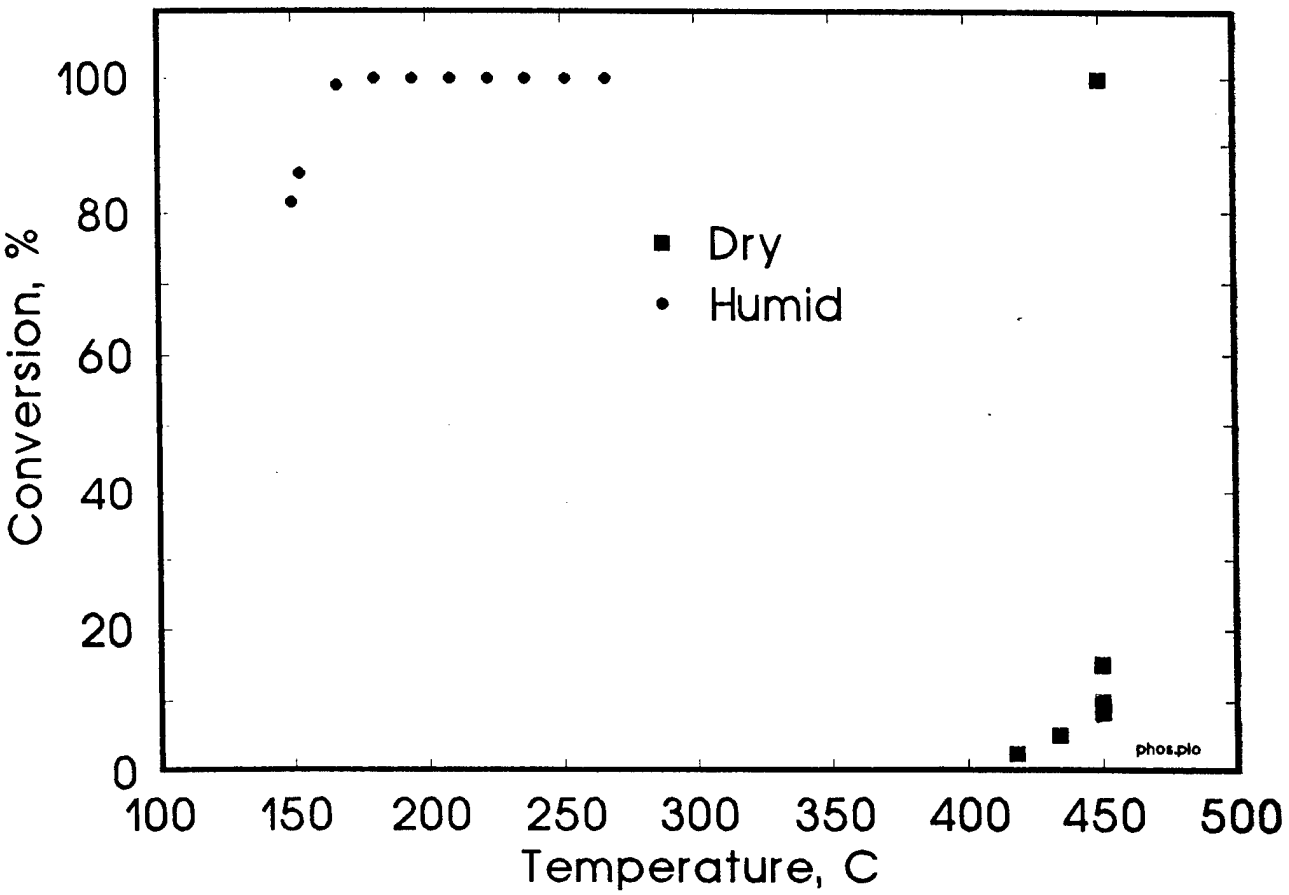


Figure 15: Conversion as a function of reaction temperature for the oxidation of 50,000 mg/m^3 phosgene in dry and humid air. Residence time = 0.80 s.

Effect of Water: The effect of water on the conversion of 50,000 mg/m^3 (11,300 ppm) phosgene as a function of reaction temperature in dry (T_{dew} ≤-40°C; 0.02 %) and humid (T_{dew} = 29°C, 4.0 %) air is reported in Figure 15. Data reported in this figure correspond to a residence time of 0.8 seconds. Results presented in this figure show that water has a significant effect on the catalytic activity. When conducting the experiment in humid air, phosgene was highly reactive, with the conversion decreasing below 99.9% at below 200° C. However, in the absence of water, the catalytic activity was significantly reduced. The reduction in activity may be due to rapid poisoning of the catalyst. Over the first hour of the run (at which time the catalyst temperature remained constant at 450°C), the conversion of phosgene decreased from 100 to about 10%.

Catalyst Deactivation: Figure 16 reports a plot of conversion as a function of time-on-stream for the oxidation of 22,100 mg/m^3 (5,000 ppm) phosgene in dry air. Data were recorded at 400°C at a residence time of 0.3 seconds. Results show that the catalyst is rapidly deactivated by phosgene, as the conversion decreases from 100% to about 50 % in one hour, and to 10% after 4 hours.

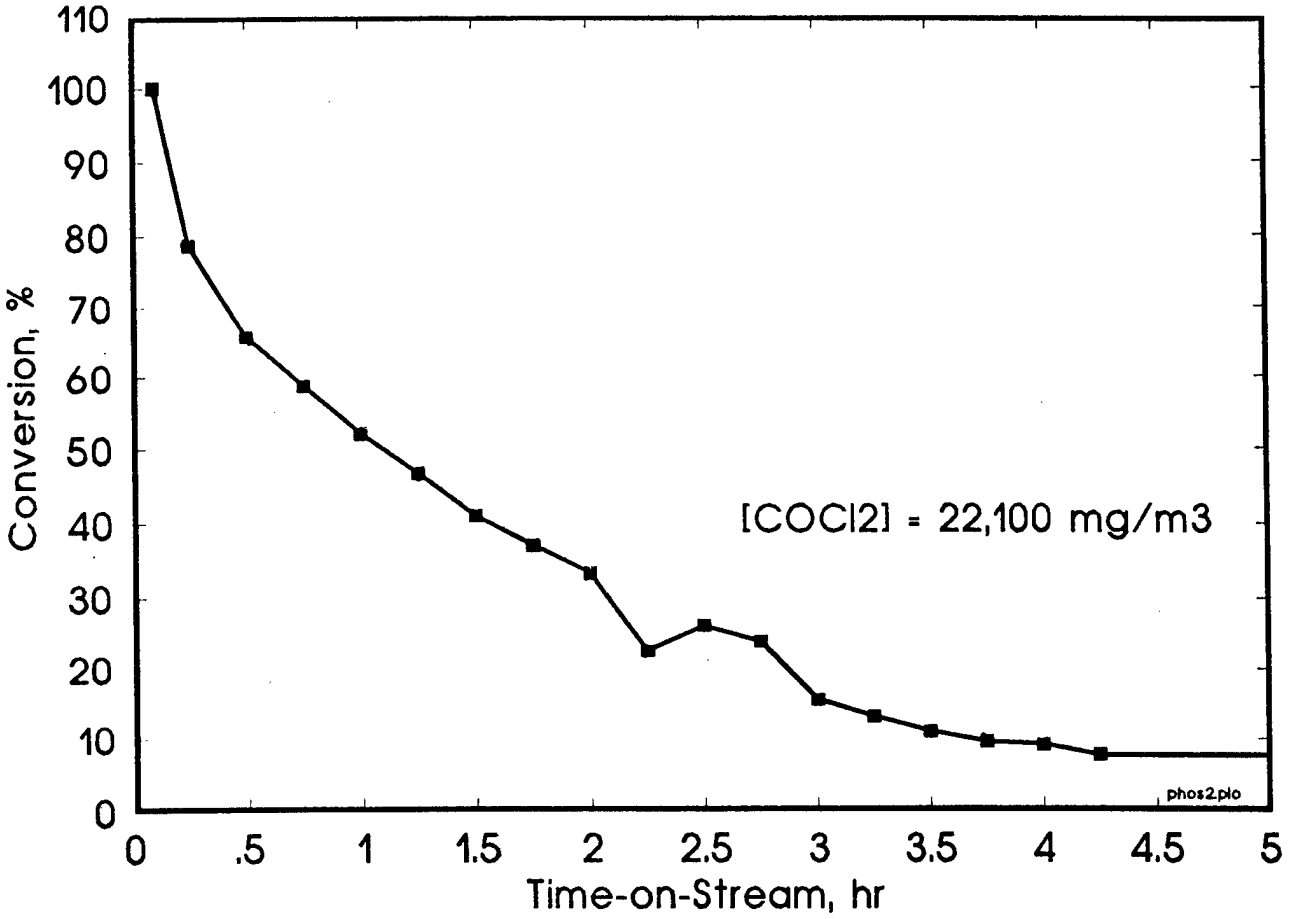


Figure 16: Conversion as a function of time-on-stream for the oxidation of 22,100 mg/m^3 phosgene in dry air at 400°C. Residence time = 0.30 s.

Reaction Products: CO_2 was the only reaction product identified via on-line gas chromatograph analyses. Dräger tubes were used to analysis the reactor effluent for Cl_2 and HCl concentrations during a test conducted with 8,840 mg/m^3 (2,000 ppm) phosgene in dry and humid air. For the test conducted in dry air, the effluent was sampled during the first 30 minutes of the test (where the conversion of phosgene was greater than 95%) due to the observed rapid deactivation of the catalyst. Under humid conditions, HCl was the predominant chlorine containing reaction product, with only traces (less than 10 ppm) of Cl_2 observed. HCl was likely formed as a result of a catalyzed hydrolysis reaction; that is, phosgene reacts with adsorbed water on the surface of the catalyst to yield CO_2 and HCl. In the absence of water, significant quantities of Cl_2 were observed. Because of the high Cl_2 concentration, the concentration of HCl could not be determined using Dräger tubes due to cross sensitivity. Acid gas reaction products are summarized in Table 7. For the test conducted in humid air, the chlorine balance is very good (92%). For the test conducted in dry air, the chlorine balance is low (74%). This may be due to chlorine adsorbed on the surface of the catalyst or the formation of HCl due to reaction with surface hydroxyls.

Table 7
Reaction product distribution during the oxidation of 2,000 ppm $COCl_2$ at 350°C

$[H_2O]$, %	$[CO_2]$, ppm	$[Cl_2]$, ppm	[HCl], ppm
2.0	2043±138	6	3680±117
>0.02	1683±218	1473±91	N/A

3.7 Oxidation of Hydrogen Cyanide.

Blank Run: A blank run was performed in order to assess the thermal stability of hydrogen cyanide. Data were recorded at 435°C employing a hydrogen cyanide feed concentration of 30,000 mg/m^3 (24,900 ppm) in dry air flowing at 50 Nml/min. No significant conversion was observed (to within experimental error) over a two hour period, indicating that hydrogen cyanide is thermally stable.

Effect of Water: The effect of water on the conversion of 30,000 mg/m^3 hydrogen cyanide in dry (T_{dew}≤-40°C) and humid (T_{dew} = 29°C) air is reported in Figure 17. Both tests employed a hydrogen cyanide feed concentration of 30,000 mg/m^3, as opposed to 50,000 mg/m^3, in order to be safely below the lower explosion limit of hydrogen cyanide. Data reported in Figure 17 shows that water has a mild inhibition effect on the oxidation of hydrogen cyanide. It is interesting to note how steep the slope of the conversion versus temperature curve is. This behavior suggests that the oxidation of hydrogen cyanide is highly non-linear in concentration. Based on results reported in Figure 17, all subsequent testing with hydrogen cyanide was performed in humid air.

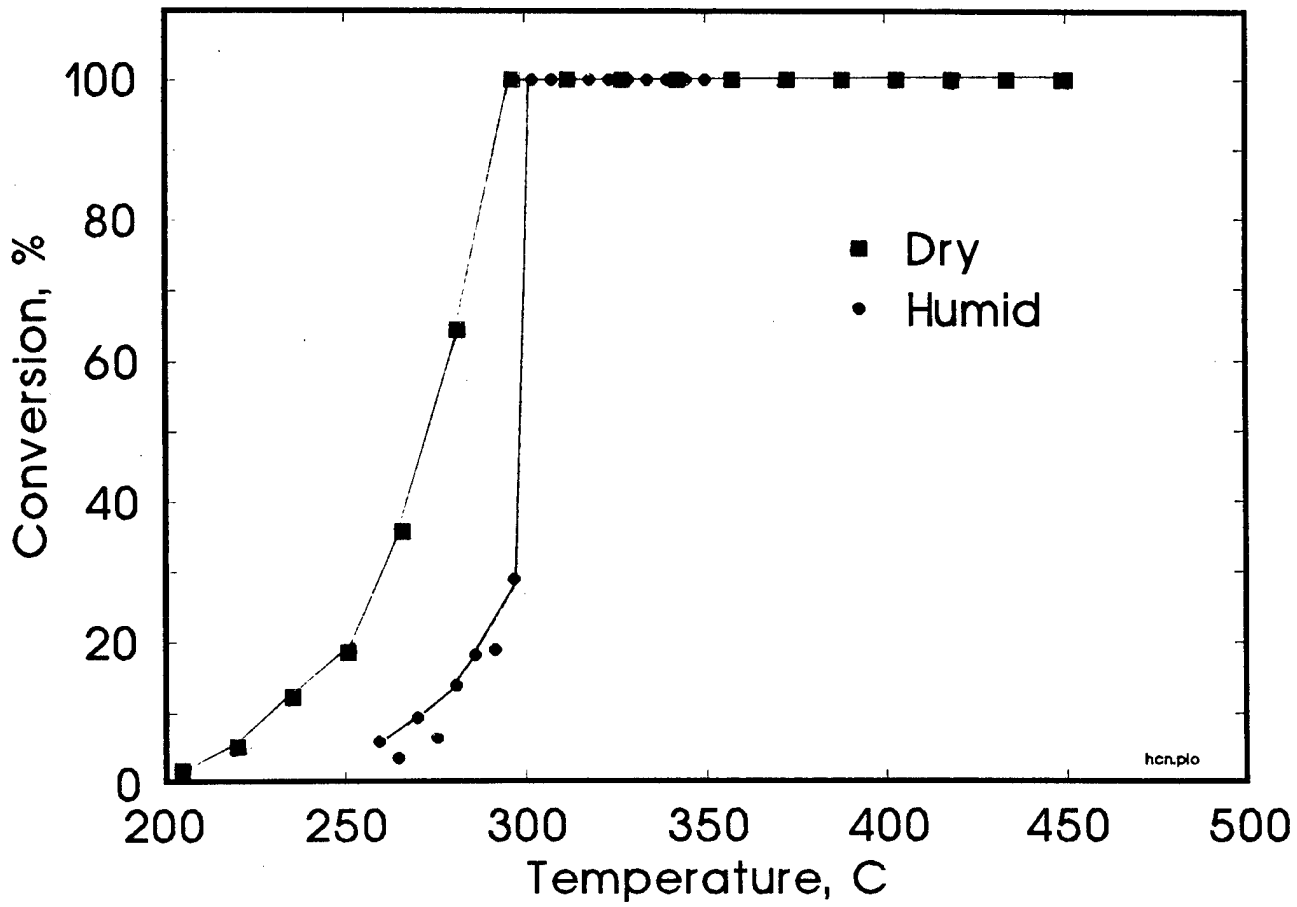
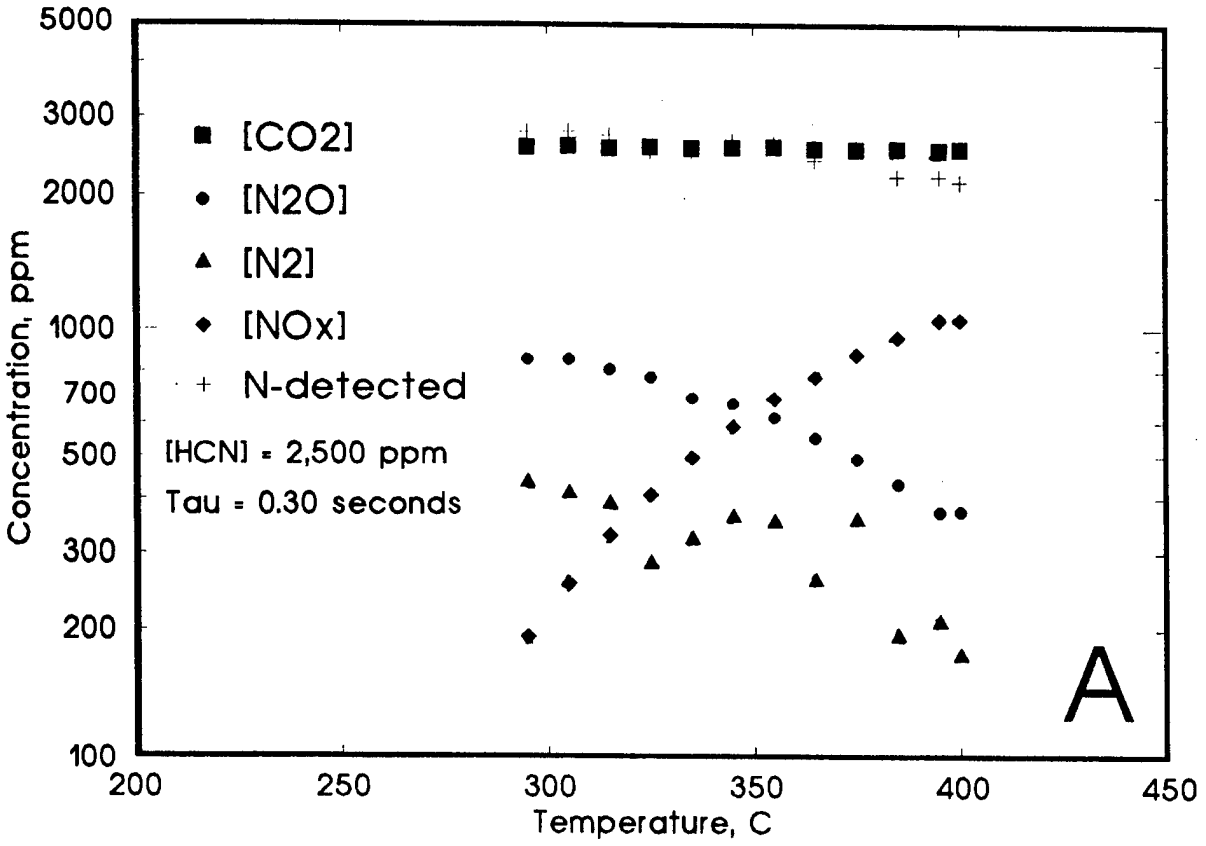


Figure 17: Conversion as a function of reaction temperature for the oxidation of 30,000 mg/m^3 hydrogen cyanide in dry and humid air. Residence time = 0.80 s.

Reaction Products: Reaction products formed during the oxidation of hydrogen cyanide may include CO, CO_2, H_2O, N_2O, N_2, NH_3, NO and NO_2. NO and NO_2 are referred to collectively as NO_x. In order to adequately assess reaction products formed during the oxidation of hydrogen cyanide, an experiment was conducted employing a hydrogen cyanide feed concentration of 2,500 ppm in 21% O_2/He. Concentrations of CO, CO_2, N_2O, N_2 and NH_3 were determined using a TCD. Concentrations of NO and NO_2 were measured using an NO-NO_x analyzer. The experiment was performed by exposing the catalyst to the reactant mix at 450°C for one hour. Following one hour, the catalyst temperature was decreased at 30°C/hr. Figure 18 reports the reaction product concentrations (A) and reaction product selectivity (B) as a function of temperature. Data are reported only for conditions where the conversion of hydrogen cyanide is greater than 99.95%. The only reaction products observed were CO_2, N_2O, N_2, NO and NO_2. At high temperatures, the oxidized reaction products (NO_x) are favored. Operation at low reaction temperatures favors the formation of the reduced products (N_2 and N_2O). However, under no conditions in which the conversion of HCN was greater than 99.9% was NO_x not observed.



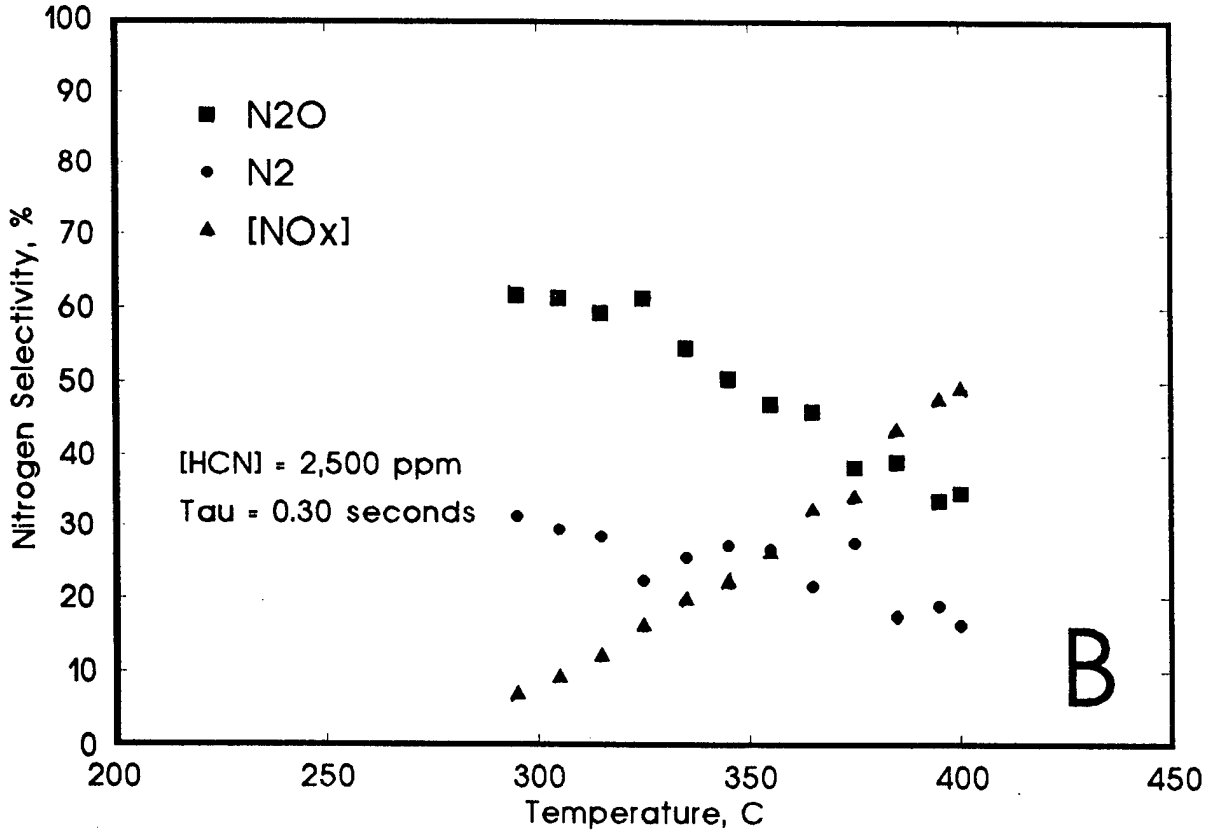


Figure 18: Reaction product concentration (A) and nitrogen-containing reaction product selectivity (B) for the oxidation of 3,000 mg/m^3 hydrogen cyanide in 21% O_2/He as a function of reaction temperature. Residence time = 0.3s.

3.8 Oxidation of Cyanogen Chloride.

Blank Run: A blank run was performed to assess the thermal stability of cyanogen chloride. Data were recorded at 450°C employing a cyanogen chloride feed concentration of 16,700 ppm (45,800 mg/m^3) in both dry and humid air flowing at 50 Nml/min. In dry air, no conversion was observed (to within experimental error) over a two hour period. In humid air, a small amount of conversion (less than 7%) was observed in a two hour period. These results indicate that cyanogen chloride is thermally stable at the above stated reaction conditions.

Effect of Water: In dry air, the catalyst was rapidly deactivated by cyanogen chloride (*vide infra*) to the extent that the standard experiment could not be reliably recorded. Figure 19 reports the conversion of 45,800 mg/m^3 (16,700 ppm) cyanogen chloride in humid air (T_{dew} = 29°C; 4.0%) as a function of reaction temperature. For temperatures above 350°C, the conversion of cyanogen chloride was greater than 99.9%. Results of this study indicate that water has a significant effect on the catalytic activity during the oxidation of cyanogen chloride.

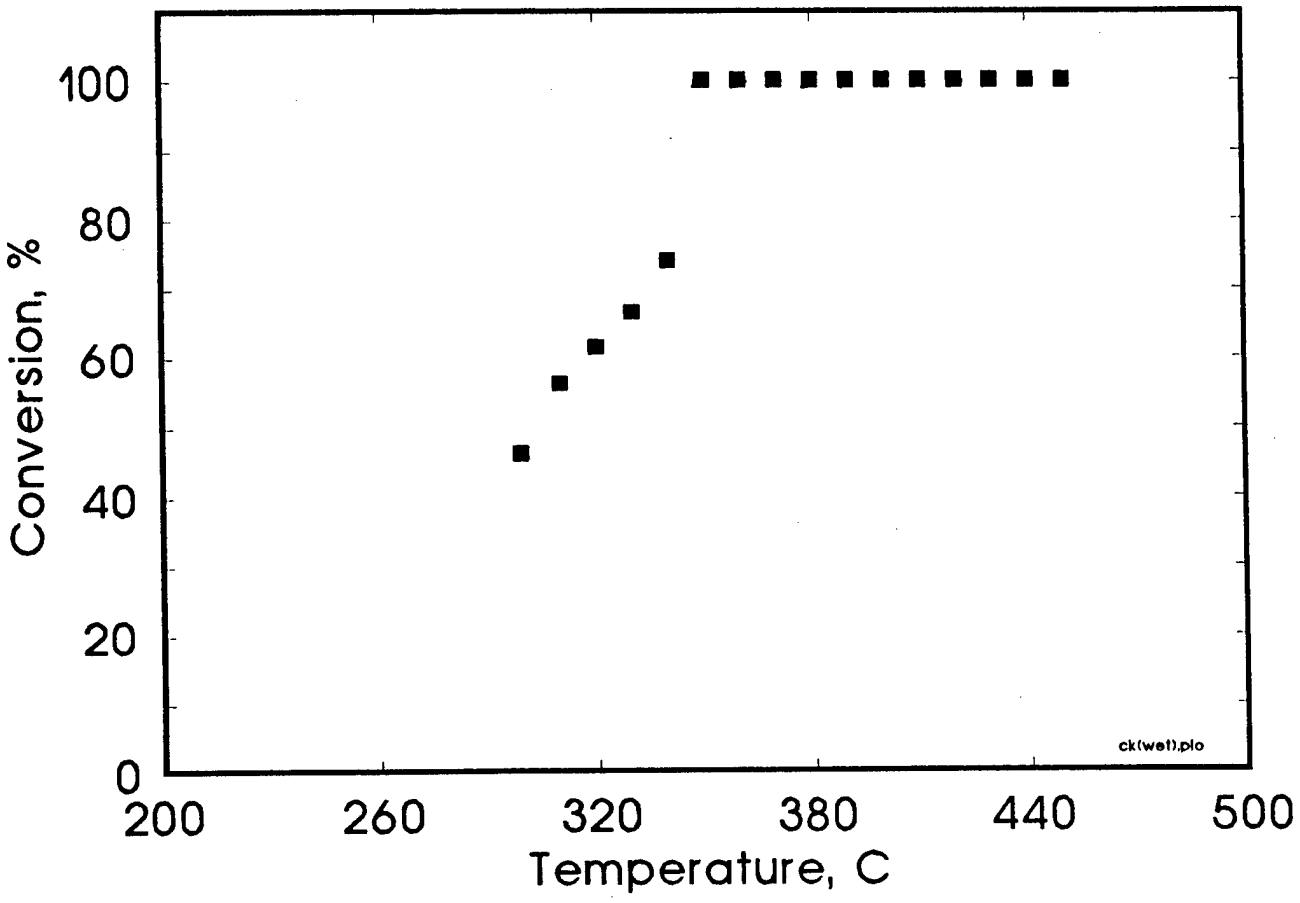


Figure 19: Conversion as a function of reaction temperature for the oxidation of 45,800 mg/m^3 cyanogen chloride in humid air. Residence time = 0.80 s.

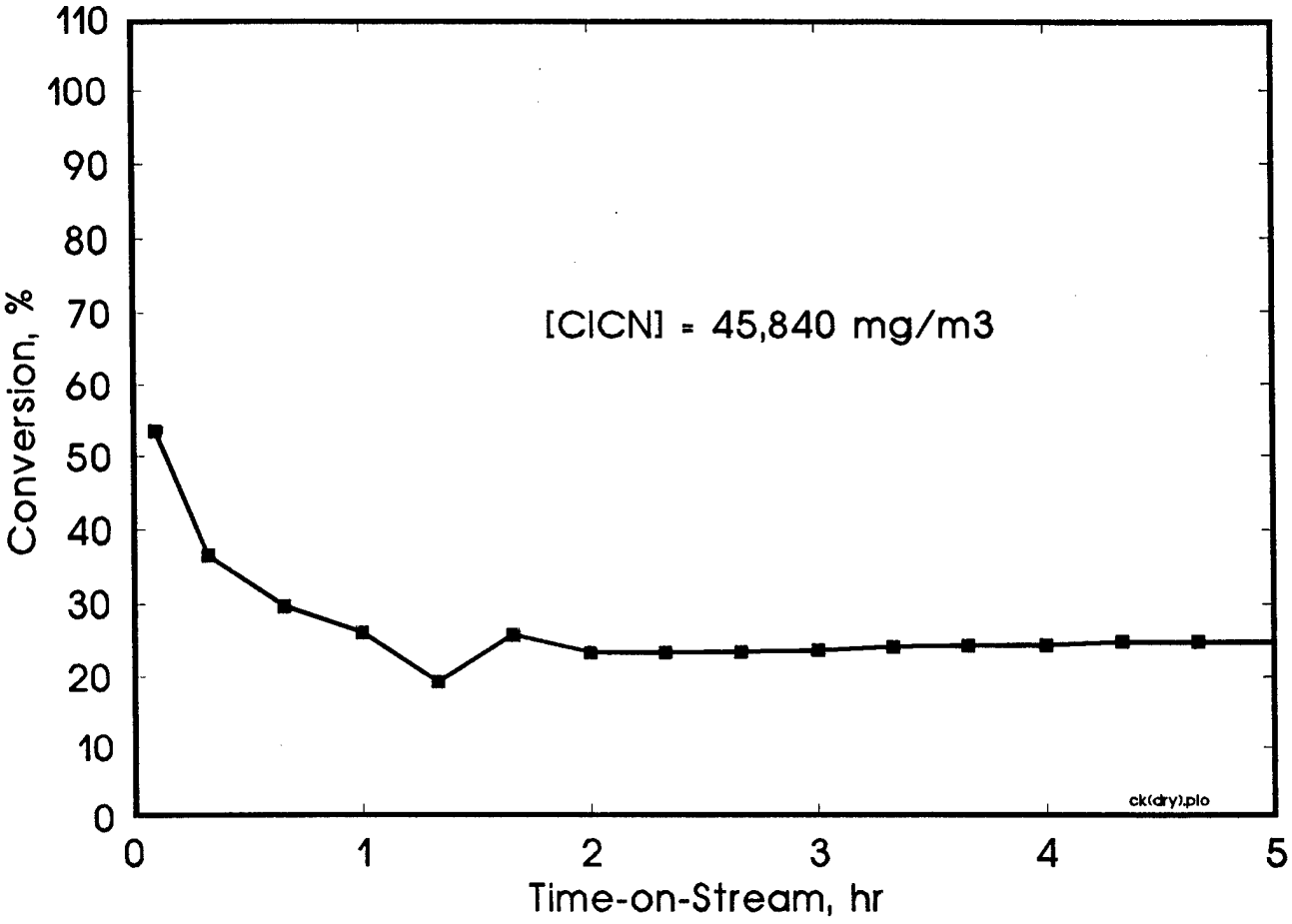


Figure 20: Conversion as a function of time-on-stream for the oxidation of 45,800 mg/m3 cyanogen chloride in dry air at 450°C. Residence time = 0.80 s.

Catalyst Deactivation: Figure 20 reports conversion as a function of time-on-stream for the oxidation of 45,800 mg/m^3 cyanogen chloride in dry ($T_{dew} \leq -40°C$) air. Data reported in this figure were recorded at 450°C at a residence time of 0.8 seconds. The catalyst rapidly deactivated over the first hour of continuous exposure, after which, the conversion remains constant at about 25% over the remainder of the run.

Reaction Products: CO_2 was the only reaction product identified via on-line gas chromatograph analysis. One unknown reaction product was observed via GC analysis at reaction temperatures below about 320°C. The unknown was identified using GC/MS techniques to be cyanogen (N≡C-C≡N). The concentrations of cyanogen were estimated not to exceed 75 ppm for a 16,700 ppm feed. Dräger tubes were used to analyze the reactor effluent for Cl_2 and HCl during exposure of the catalyst to 2,000 ppm cyanogen chloride at 400°C. When conducting the test in humid air (T_{dew} = 18°C, 2.0 %), HCl was the primary chlorine-containing reaction product observed, with only minimal amounts of Cl_2 detected. However, when conducting the experiment in dry air, significant quantities of Cl_2 were observed. Due to cross sensitivity, with Cl_2, the concentration of HCl could not be determined. Acid gas reaction product data are summarized in Table 8.

Table 8
Reaction product distribution during oxidation of 2,000 ppm ClCN at 400°C.

$[H_2O]$, %	$[CO_2]$, ppm	$[Cl_2]$, ppm	[HCl], ppm
2.0	1896±43	15±7	1450±75
>0.12	1768±106	736±61	N/A

3.9 Oxidation of Arsine.

Blank Run: A blank run was performed in order to assess the thermal stability of arsine. Data were recorded by flowing at 50 Nml/min 49,000 mg/m^3 (14,100 ppm) arsine in dry air through the catalyst-free reactor at 350°C and decreasing the reactor temperature at 30 °C/hr. Results of this test are reported in Figure 21. Results demonstrate that arsine is not thermally stable at reaction temperatures greater than 300°C and is in agreement with the information provided in the Material Safety Data Sheet (MSDS) for arsine. The thermal decomposition product is believed to be As_2O_3, based on information contained in the MSDS.

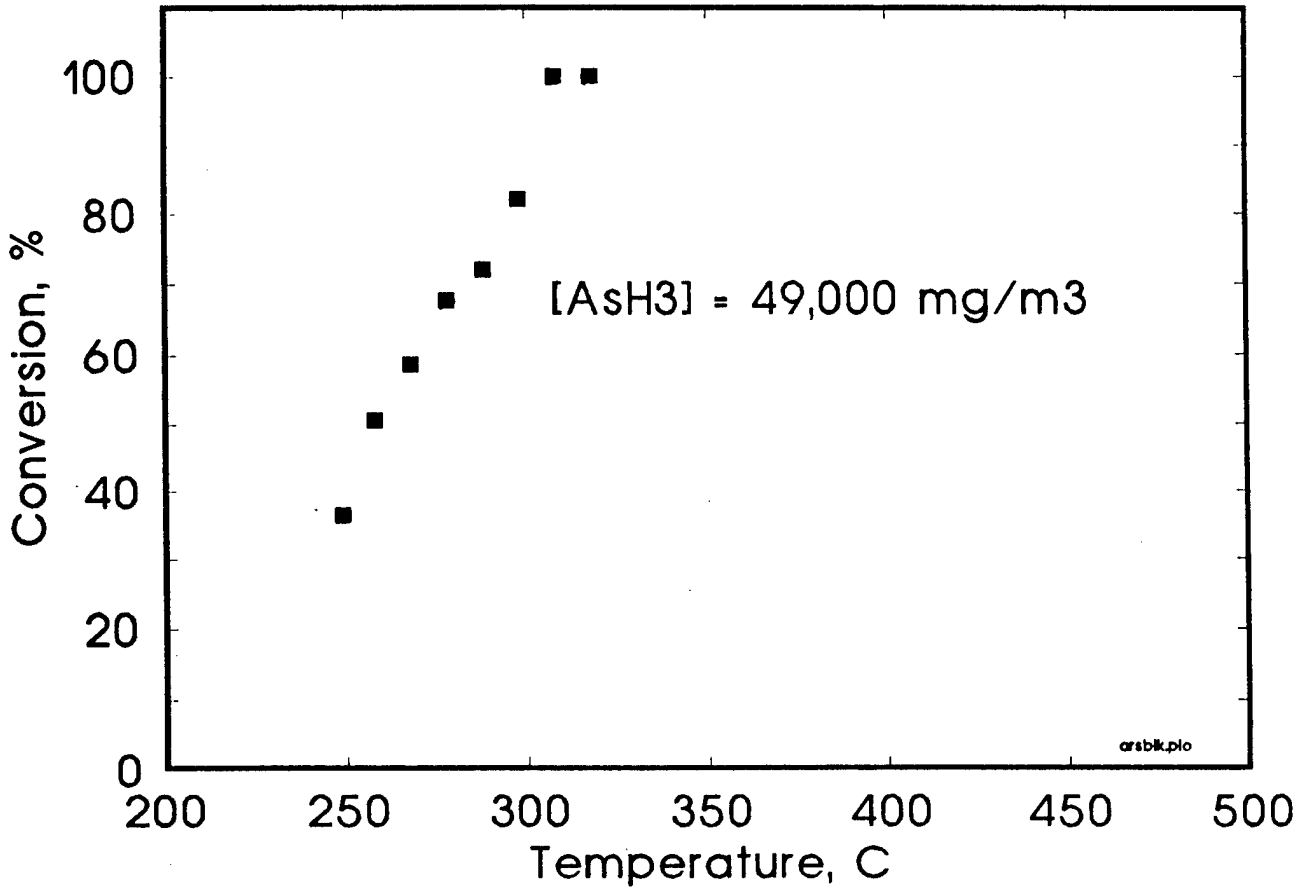


Figure 21: Conversion as a function of reaction temperature for the oxidation of 49,000 mg/m^3 arsine in dry air flowing at 50 Nml/min through a catalyst-free reactor.

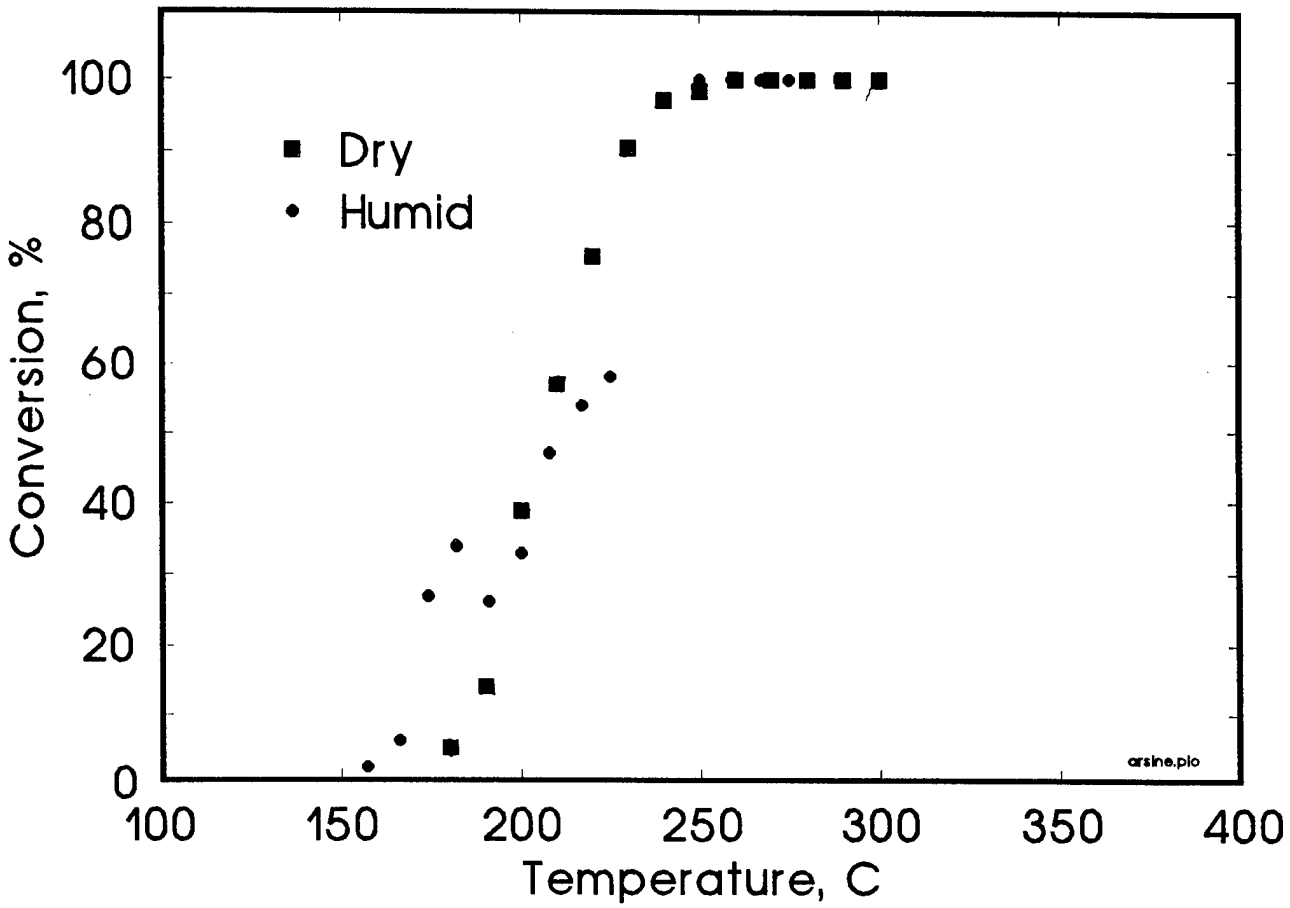


Figure 22: Conversion as a function of reaction temperature for the oxidation of 50,000 mg/m^3 arsine in dry and humid air. Residence time = 0.80 s.

Effect of Water: The effect of water on the conversion of 50,000 mg/m^3 (14,400 ppm) arsine as a function of reaction temperature in dry ($T_{dew} \leq -40°C$) and humid (T_{dew} = 29° C) air is reported in Figure 22. Data presented in this figure correspond to a residence time of 0.8 seconds. Results presented in this figure indicate (1) that arsine is highly reactive and (2) that to within experimental error, water has no effect on the catalytic activity.

Reaction Products: No reaction products were observed during on-line GC analysis. Examination of the spent catalyst via XPS revealed the presence of significant quantities of As_2O_3.

3.10 Oxidation of Chloropicrin.

Blank Run: A blank run was performed to assess the thermal stability of chloropicrin. Data were recorded at 450°C employing a chloropicrin feed concentration of 50,000 mg/m^3 (6,800 ppm) in humid air (T_{dew} = 29°C; 4.0%) flowing at 50 Nml/min. No conversion was observed, indicating that chloropicrin is thermally stable at the above stated reaction conditions.

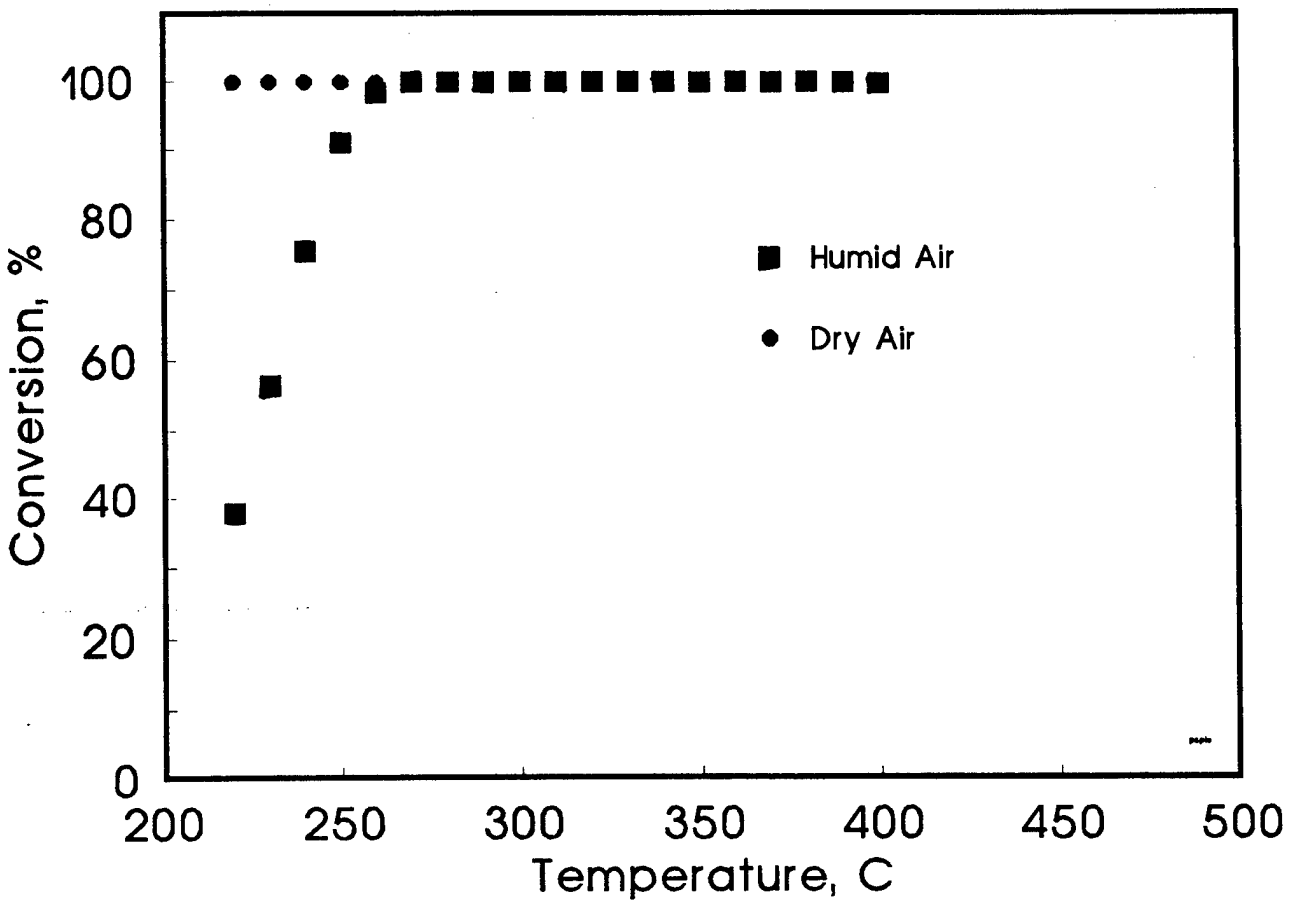


Figure 23: Conversion as a function of reaction temperature for the oxidation of 50,000 mg/m^3 chloropicrin in dry and humid air. Residence time = 0.80 s.

Effect of Water: Figure 23 reports the conversion of 44,400 mg/m^3 (6050 ppm) chloropicrin in dry (T_{dew} < -40°C; 0.02% H_2O) and humid (T_{dew} = 29°C; 4.0% H_2O) air as a function of reaction temperature. The presence of water in the feed stream inhibited the reactivity of the catalyst. As a result, all further testing with chloropicrin were conducted in humid air.

Catalyst Deactivation: The stability of the catalyst was evaluated by exposing it to 44,400 mg/m^3 (6,050 ppm) chloropicrin at 350°C in humid (T_{dew} = 13°C; 1.4% H_2O) air at a residence time of 0.16 s. The above process conditions were maintained for 22 hours. During the run, the conversion of chloropicrin was greater than 99.9%, indicating that deactivation was not significant.

Reaction Products: During the oxidation of chloropicrin, three reaction products were observed during FID analysis of the reactor effluent stream. One of these products was identified via GC/MS as carbon tetrachloride. Carbon tetrachloride was observed only at reaction temperatures below 300°C. The remaining two compounds were also observed below 300°C and could not be identified. The concentration of these compounds were estimated not to exceed 50 ppm over the entire temperature range.

3.11 Oxidation of Diphosgene.

Blank Run: A blank run was performed to assess the thermal stability of diphosgene. Data were recorded by exposing the catalyst-free reactor to 25,000 mg/m^3 diphosgene in dry air flowing at 50 Nml/min at 300°C. At this temperature, diphosgene was completely converted, with the major reaction product being phosgene. The reaction temperature was then decreased at 30°C/hr. Diphosgene was only observed in the reactor effluent stream at reaction temperatures below 150°C. This result is consistent with thermal stability results reported in the diphosgene MSDS. Because of the low thermal stability of diphosgene, no further testing was performed.

4. SUMMARY

Thermal Stability: The majority of the light gases evaluated in this study possessed adequate thermally stable at 400°C. However, three of the light gases, namely perfluoronitrosomethane, arsine and diphosgene, decomposed readily at reaction temperatures above 300°C. Of the three, only perfluoronitrosomethane decomposed to yield CO_2. Arsine likely (based on information contained within the MSDS) decomposed to As_2O_3, while the thermal decomposition of diphosgene yielded phosgene. Both As_2O_3 and phosgene are highly toxic.

Effects of Water: For the majority of the light gases tested, water had a significant effect on the performance of the catalyst. The addition of water to the feed stream resulted in a significant inhibition effect for the oxidation of perfluorocyclobutene, methoxyfluorane, trifluoronitrosomethane and chloropicrin. However, the addition of water to feed streams containing phosgene and cyanogen chloride greatly enhanced the catalytic activity. Results obtained during this testing demonstrate that water will have significant design implications and therefore its effects warrant further investigation.

Reaction Products: The preferred reaction products for the oxidation of light gases are CO_2, N_2, H_2O and mineral acids (SO_2, HF and HCl). CO_2, N_2 and H_2O are innocuous, and acid gases can be removed via conventional acid gas scrubbing techniques. In the case of methoxyfluorane, perfluoronitrosomethane, hydrogen cyanide, cyanogen chloride and chloropicrin, the reactant chemicals were not completely destroyed to the desired breakdown products over the entire temperature range. Of these, only hydrogen cyanide appears to present a significant challenge. While undesired breakdown products were observed for the other light gases listed above, these products are either believed to be non-hazardous (e.g. perfluoro*nitro*methane) or can be eliminated by increasing the reaction temperature. In the case of hydrogen cyanide, significant amounts of NO_x are generated. This presents a special problem in that once formed, NO_x cannot be readily scrubbed from air streams. Based on this result, there is a need to identify a catalyst capable of destroying hydrogen cyanide without the formation of NO_x.

Reactivity: In humid air streams, perfluorcyclobutene required the greatest temperature and longest residence time to achieve 99% reduction. Based on data presented in conversion-versus-temperature curves, 99% destruction of perfluorocyclobutene at a residence time of 0.80 seconds will require a reaction temperature of approximately 500°C. 99% destruction of all remaining compounds could be achieved at reaction temperatures below 400°C. In dry air, both phosgene and cyanogen chloride deactivated the catalyst at a rate which prohibited us from measuring conversion-versus-temperature curves. Reactivity results point to the need to identify catalysts which are more reactive towards perfluorocyclobutene and at the same time stable towards the destruction of cyanogen chloride and phosgene.

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