Copyright Warning & Restrictions

The copyright law of the United States (Title 17, United States Code) governs the making of photocopies or other reproductions of copyrighted material.

Under certain conditions specified in the law, libraries and archives are authorized to furnish a photocopy or other reproduction. One of these specified conditions is that the photocopy or reproduction is not to be "used for any purpose other than private study, scholarship, or research." If a, user makes a request for, or later uses, a photocopy or reproduction for purposes in excess of "fair use" that user may be liable for copyright infringement,

This institution reserves the right to refuse to accept a copying order if, in its judgment, fulfillment of the order would involve violation of copyright law.

Please Note: The author retains the copyright while the New Jersey Institute of Technology reserves the right to distribute this thesis or dissertation

Printing note: If you do not wish to print this page, then select "Pages from: first page # to: last page #" on the print dialog screen



The Van Houten library has removed some of the personal information and all signatures from the approval page and biographical sketches of theses and dissertations in order to protect the identity of NJIT graduates and faculty.

ABSTRACT

Selective NO Absorption from Gas Streams with Tertiary Organic Hydroperoxide Solutions

by Huihong Ao

The selective removal of nitric oxide from gas streams investigated using 3,6-dimethyl-3-octyl hydroperoxide, was p-menthane hydroperoxide, pinane hydroperoxide, and cumene hydroperoxide in solutions of n-hexadecane (cetane). The influence of different parameters such as temperature, gas stream flow rate (or residence time), and concentration of hydroperoxide compounds on efficiency of NO removal was The basis of this research was to evaluated. duplicate atmospheric reactions between hydroperoxides and NO in order to produce NO2. We succeeded in removing NO from qas streams, but failed to produce NO₂. NO reacted with the hydroperoxides to produce nitrates. These nitrates are easily hydrolyzed with ammonium hydroxide to ammonium nitrates and alcohols. The hydroperoxides used in this study were selected to be inexpensive and commercially available, low vapor pressure to avoid loss of reagent when contacted with hot flue gas, and easily regenerated. This research was conducted in a scrubbing reactor system with associated feed and products flow measurement equipment. The reactor consisted of a fritted disk through which a gas stream of NO in helium was bubbled into the hydroperoxide solution. Feed and effluent gas stream were analyzed using a gas chromatograph (GC) with a thermal conductivity detector (TCD) or a chemiluminescent NO_x analyzer. A Fourier transform infrared spectrometer (FTIR) was used to determine organic product distribution and an ion chromatograph (IC) was used to measure inorganic products from the hydrolysis, and from an aqueous scrubber used to detect NO_2 .

Higher rates of oxidation were obtained with cumene and pinane hydroperoxide than with the other two organic hydroperoxides tested. The highest rates of NO removal were obtained at the highest temperatures, highest concentrations, and lowest gas flow rates. With p-menthane hydroperoxide as the oxidizer, the main product is p-menthane nitrate. No NO_2 was produced. Consequently, it is assumed that the main product from the other hydroperoxides is also the nitrate. In this research, excellent nitrogen mass balance were obtained to within 100 + 10% with p-menthane hydroperoxide. Again it is assumed that equivalent material balances are achieved with the other hydroperoxides.

p-Menthane nitrate can be efficiently denitrated in dilute aqueous ammonia to produce ammonium nitrate and menthanol. Some experiments were conducted with hydroperoxylated polypropylene fibers as a solid oxidizer to remove NO. High rates of removal of NO was achieved at similar conditions to those used with the liquid hydroperoxides, namely, high temperature, high concentration of the hydroperoxide group, and low gas flow rate (high residence time).

Selective NO Absorption from Gas Streams with Tertiary Organic Hydroperoxide Solutions

by

Huihong Ao

A Dissertation

Submitted to the Faculty of the Graduate Division of the New Jersey Institute of Technology in Partial Fulfillment of the Requirements for the Degree of Master of Science in Applied Chemistry Department of Chemical Engineering, Chemistry and Environmental Science

January 1992

APPROVAL SHEET

Title of Thesis : Selective NO Absorption from Gas Streams with Tertiary Organic Hydroperoxide Solutions

Name of Candidate : Huihong Ao

Master of Science in Applied Chemistry, 1991

Thesis and Abstract Approved : Date Heñry Shaw Ph.D. Professor Thesis and Abstract Approved : Date 'Howard Perlmutter Ph.D. Professor Thesis and Abstract Approved : Date /Barbara Kebbékus Ph.D. Professor

BIOGRAPHICAL SKETCH

- Author: Huihong Ao
- Degree: Master of Science in Applied Chemistry
- Date: January, 1992

Undergraduate and Graduate Education:

Master of Science in Applied Chemistry, New Jersey Institute of Technology, Newark, NJ, 1992 Bachelor of Science in Chemical Engineering, South China Institute of Technology, Guangzhou, P. R. China, 1985

Major: Applied Chemistry

ACKNOWLEDGMENT

The author wishes to express her sincere appreciation to her co-advisor, Professor Henry Shaw for his guidance, encouragement, and enlightened discussions. Special thanks are given to coadvisor, Professor Howard Perlmutter for his significant guidance and help in experimental approach and for his advice on organic chemistry and to Professor B. Kebbekus for serving as member of the committee. Special thanks are also given to Mr. C. Brockway and Ms. G. San Agustin for their advice and help in instrumental application and in developing experimental method, Mr. C. Wenger for synthesizing the 3,6-dimethyl-3-octyl hydroperoxide and doing iodometric analyses, as part of a master of engineering science project and Mr. W. Barlettano for his help in studying the denitration process.

The author acknowledges with much appreciation the help she received from her colleague Jonathan Yang.

The author also acknowledges support from NJIT's Hazardous Substance Management Research Center for support of this study.

V

TABLE OF CONTENTS

	Page
1	INTRODUCTION1
	1.1 NO _x Formation and Sources1
	1.1.1 Fuel combustion2
	1.1.2 Lightning
	1.1.3 Microbial activity in soils
	1.2 Effects of NO _x 4
	1.2.1 Acid precipitation4
	1.2.2 Health effects4
	1.3 Technologies for NO _x Control
	1.3.1 Combustion modification7
	1.3.2 Flue gas cleaning8
2	LITERATURE REVIEW12
3	EXPERIMENTAL
	3.1 Material
	3.1.1 Organic hydroperoxides
	3.1.2 Gases
	3.1.3 Isobutyl nitrate and tertiary butyl nitrite
	standards for IR calibration
	3.1.4 Hexadecane solvent
	3 2 Annaratus
	2.2 Experimental Drogodure for Carubbing
	3.3 Experimental Procedure for Deribustion
	3.4 Experimental Procedure for Denitration
	3.5 Analytical Techniques
	3.5.1 Gas chromatograph27

	3.5.2 Chemiluminescent NO _x analyzer
	3.5.3 Fourier transform-infrared spectrometer
	3.5.4 Ion chromatograph
4	RESULTS AND DISCUSSION
	4.1 Effect of Operating Parameters on NO Removal
	4.1.1 NO conversion as a function of reaction time36
	4.1.2 Effect of temperature on NO oxidation40
	4.1.3 Effect of tertiary organic hydroperoxide
	concentrations in cetane on NO oxidation43
	4.1.4 Effect of gas flow rate on NO oxidation43
	4.1.5 Color change in the reaction
	4.2 Products Analysis50
	4.3 Nitrogen Balance61
	4.3.1 Definition of nitrogen balance
	4.3.2 Calculation of nitrogen balance
	4.4 Denitration Studies67
5	CONCLUSIONS
6	RECOMMENDATIONS
7	HYDROPEROXYLATED POLYPROPYLENE FIBER STUDIES
8	REFERENCES

Page

LIST OF TABLES

Ta	able Page
1	Key Reactions of Nitrogen-Oxygen Mixtures at High Temperatures2
2	Fraction of Reaction of RO ₂ + NO Producing Alkyl Nitrates for Individual Alkylperoxy Radicals at Room Temperature and 735-740 Torr Total Pressure19
3	Analytical and Physical Data for Hydroperoxides24
4	Effect of Temperature on NO Scrubbing with Organic Hydroperoxide41
5	Effect of Organic Hydroperoxide Concentration on NO Scrubbing
6	Effect of Gas Flow Rate on NO Scrubbing with Organic Hydroperoxides47
7	NO-removing Ability of Hydroperoxides
8	Data for Model Nitrates and Nitrites
9	Raw Data for Calculation of Nitrogen Balance65
10	Nitrogen Balance
11	. NO Removal with Hydroperoxylated Polypropylene Fiber72

LIST OF FIGURES

Figure Pa	ıge
l Profiles of Selected Reactants and Products for a Typical Smog Chamber Run	.6
2 Structures of Four Organic Hydroperoxides	11
B Flow Schematic of NO _X Absorption Unit	26
Gas Chromatograph Peak Resolution	29
5 Calibration Curve for NO Concentration	30
5 FTIR Spectrum of Isobutyl Nitrate Standard	32
FTIR Spectrum of Tertiary butyl Nitrite Standard	33
Typical IC Chromatogram	35
NO Conversion, vs., Time at 90 ⁰ C with 0.296 M p-Menthane Hydroperoxide	37
.0 NO Conversion, vs., Time at 90 ⁰ C with 0.230 M Pinane Hydroperoxide	38
.1 NO Conversion, vs., Time at 90 ⁰ with 0.505 M Pinane Hydroperoxide	39
2 Conversion of NO in Organic Media	45
3 Cumene Hydroperoxide Concentration, vs., NO Conversion	46
4 Ion Chromatogram from Blank Water Sample	51
5 Ion Chromatogram from Aqueous Scrubbing Solution	52
6 Ion Chromatogram from Aqueous Scrubbing Solution	53
7 Isobutyl Nitrate Infrared Calibration Curve	55
8 Tertiary butyl Nitrite Infrared Calibration Curve	56
9 FTIR Spectra of Fresh Solution and Solvent	58
0 FTIR Spectra of Reacted Solution and Solvent	59

Figure

21	Comparison of FTIR Spectra from Fresh and Reacted Solution
22	Composite Spectrum Consisting of the Difference between the Starting and Final Solution Spectrum62
23	Breakthrough Curve for Hydroperoxylated Polypropylene Fiber at 80 [°] C74

Page

1 INTRODUCTION

Nitrogen oxides (NO_x) are mixtures of compounds of nitrogen and oxygen, namely, N_2O , NO, N_2O_3 , NO₂, N_2O_4 , and N_2O_5 , generally found in effluents from combustion sources. The predominant NO_x are NO and NO2. They are formed as a result of the reactions of atmospheric nitrogen with atmospheric oxygen at high temperatures. Also, large quantities of NO_x are formed from the oxidation of nitrogen compounds found in fuels, or in wastes being incinerated. More than 90% of NO_x emitted from stationary combustion sources consist of NO which is relatively insoluble in inorganic aqueous solutions. Acidic deposition is related primarily to the emissions of sulfur dioxide (SO_2) and nitrogen oxides (NO_x). In 1985, anthropogenic sources in the United States contributed 19 Tg of NO_x emissions. Emissions of NO_x are estimated to have increased steadily during the period between 1900 and The increase in NO_x emissions resulted from the rise in 1970. fuel consumption, particularly in power plants and motor vehicles 1991). The object of this research is to find a novel (Irving, way to remove NO from gas mixtures using essentially unexplored methods such as organic oxidizing agents.

1.1 NO_x Formation and Sources

Nitrogen oxides are emitted primarily as nitric oxide (NO) from a variety of high temperature sources. The estimated emissions of NO_X have large uncertainties associated with them. About 70-90% atmospheric NO_X emission are from anthropogenic sources in

the world (Singh, 1987).

1.1.1 Fuel combustion

Oxides of nitrogen (NO_x) are produced in all combustion processes using air as the oxidizer. At flame temperatures, the combination of atmospheric oxygen and nitrogen results in the formation of nitric oxide (NO). The mechanism of formation of NO from nitrogen and oxygen follows the chain reaction sequence first postulated by Zeldovich (1946) for the $H_2-O_2-N_2$ reaction system and confirmed by shock tube studies on N_2-O_2 mixtures (Glich, et al., 1957). Equations 1-3 in Table 1 show this chain reaction sequence.

Besides the atomic chain route, NO can also be formed by reaction 4 (Shaw, 1974).

Reaction		Rate constants cm ³ mole ⁻¹ sec ⁻¹
$O_2 + M = 20 + M$	(1)	$k_2 = 1.36 * 10^{14} \exp [-75,400/RT]$
		13
$0 + N_2 = NO + N$	(2)	$k_{-2} = 3.10 * 10^{-5} \exp \left[-334/RT\right]$
		٩
$N + O_2 \longrightarrow NO + O$	(3)	$k_3 = 6.43 * 10^9 T \exp [6250/RT]$
		11 1/0
OH + N = NO + H	(4)	$k_4 = 7.25 * 10^{11} T^{1/2}$
		مین وید جه هند باله ها ها ها ها ها ها ها ها ها بنه بنه منه بنه منه می مید بنه مه هم بنه مه هه منه منه ها ها ها

Table 1. Key Reactions of Nitrogen-Oxygen Mixtures at High Temperatures

 k_2 is the forward reaction constant of equation 2. k_{-2} is the reverse reaction constant of equation 2, and so on. M is a third body. Source: Shaw, 1974.

1.1.2 Lightning

The major natural source of NO_x is caused by the effect of atmospheric lightning on atmospheric oxygen and nitrogen. The temperature of a column of air exposed to atmospheric lightning is a function of energy deposition of the lightning. For a typical energy deposition of about 10^5 J/m, the column of air immediately surrounding the charge is heated to temperature on the order of 30,000 K. At temperatures above 2,300 K, NO is in thermodynamic equilibrium with N₂ and O₂. As the temperature of the heated air drops below 2,000 K, NO "freezes" as a stable compound.

The total global production of NO due to atmospheric lightning is the product of two terms: 1) The yield of NO per energy input or lightning (J) or the NO per lightning flash, and 2) the total energy deposited by lightning or the lightning flash frequency (Levine, et al., 1984).

1.1.3 Microbial activity in soils

It has been found from field flux measurements and laboratory experiments that soil microorganisms may also produce appreciable amounts of NO. To quantify the rate of production of NO, a series of laboratory experiments were performed using two of the most common bacteria found in soils, Nitrosomonas Europaea and Alcaligenes Faecalis. The results indicate that nitrification is an aerobic process in which ammonium cations are oxidized to nitrite and nitrate anions. NO and N_2O are direct or indirect intermediates of this pathway (Levine, et al., 1984).

1.2 Effects of NO_X

1.2.1 Acid precipitation

The increasing acidity of precipitation is having a serious impact on soil, vegetation, surface water, biological systems, and structures of the earth. The U.S. National Acid Precipitation Assessment Program (NAPAP) was implemented in 1980 to conduct research and assess the complex causes and effects of acid deposition. NAPAP had two primary objectives. First, it sought to fill many gaps in the scientific understanding of acid deposition. Second, the program developed methods and evaluated the consequences of alternative acid deposition control strategies (Isom, et al., 1984).

1.2.2 Health effects

The oxides of nitrogen are not very active biologically. At exposures well above a few ppm, NO_2 causes lung damage of various types, including bronchial damage reminiscent of that from SO_2 , though less severe, and acute pulmonary edema, an effect characteristic of ozone. Since atmospheric levels only rarely reach a half ppm (1000 ug/m³), there has historically been little concern over the direct health effects of NO_2 . This view has recently been questioned by the findings from a major observational study conducted in Chattanooga. It was found that certain portions of the population had decreased ventilatory function and increased respiratory illness in neighborhoods near a factory that manufactures TNT. This unusual situation provided a test area with very low NO_2 levels ranging from 0.06 to 0.109 ppm (113-205 ug/m³). These NO_2 levels are of the same general magnitude as the

higher ambient concentrations experienced in many cities. Consequently, if further pursuit of these observations confirm the results, then we need to consider NO_2 in a new light (Lynn, 1976).

Air pollution alerts due to ozone and peroxyacetyl nitrate (PAN) may increase the rate of O_3 formation by releasing NO_2 . PAN is thermally unstable and may contribute to O_3 formation downwind of urban areas by transporting NO_x , and then decomposing into peroxyacetyl radicals and NO₂ as shown in Figure 1, which is similar to diurnal cycle (Finlayson-Pitts, 1986). Thus, NO₂ important because, as part of the diurnal cycle, it is is the precursor to ozone formation. Ozone adversely affects the health the elderly and the very young through its impact on of the respiratory system.

The reason NO_2 rather than NO is used as a standard for health effect studies is because all NO is oxidized to NO_2 in the atmosphere. The reaction rate between NO and oxygen is very slow (equation 5), but if given enough time, all NO oxidizes to NO_2 in the atmosphere (Finlayson-Pitts, 1986).

$$2NO + O_2 - 2NO_2$$
 (5)

1.3 Technologies for NO_x Control

Emissions of NO_X have become a serious environmental problem. It is necessary to control the NO_X from flue gases in order to prevent human respiratory disease, acid rain, and comply with federal and local regulations.

In the past few years, a variety of processes have been



Figure 1. Profiles of Selected Reactants and Products for a Typical Smog Chamber Run

proposed to eliminate this problem. These processes can be summarized as follows.

1.3.1 Combustion modification

a. Low NO_{X} furnace design

Various furnace designs have been proposed to lower the NO_X emission such as tangentially fired boiler. Traditional cyclone furnaces produced high concentrations of NO_X in flue gas. Because the temperature of heat sinks of tangential fired furnace is almost equal to the temperature of furnace flame, it reduces thermal NO_X formation by 50% to 60% (Maulbetsch, 1981).

b. Flue gas recirculation

Flue gas recirculation is an effective method of reducing thermal NO_X . The recirculated flue gas lowers the flame temperature and the oxygen content in combustion. According to Jahnig and Shaw (1981) flue gas recirculation reduces thermal NO_X formation by 20-30%.

c. Air-fuel staging in the combustion chamber

Thermal NO_x formation can be reduced by operating the combustor in a fuel rich mode, followed by interstage cooling and burnout of the uncombusted compounds with excess air. Incomplete combustion in the first stage lowers thermal NO_x formation. The second stage uses excess air to complete the combustion, reduce the combustion temperature and lower the thermal NO_x formation (Bienstock, 1972). Alternatively, another method of interstage cooling can be used in order to avoid a large excess of stoichiometic air.

1.3.2 Flue gas cleaning

a. Selective noncatalytic reduction

 NO_x can be reduced to N_2 and H_2O by introducing NH_3 into the effluent gas from a combustor at 930 to 990^OC. The major disadvantages of this process are the narrow temperature window, the need for well mixed NH_3 and the possibility that NH_3 may break through (Flagan and Seinfeld, 1988).

b. Selective catalytic reduction (SCR)

This process operates in a manner similar to the thermal process except that a catalyst is used. The reactions occur at a much lower temperature of 300 to 400° C. There are commercial catalysts containing noble metals or vanadium/titanium that can reduce NO_X by 90% for the former, and 80% for the latter. Current research is concerned with using zeolites to catalyze the reaction of NO_y with NH₃ (Makansi, 1988).

c. Adsorption by solids

A number of activated carbon processes have been proposed to remove NO from flue gas. Copper oxide is also an effective adsorbent. Technologies of adsorbent regeneration and SO₂ removal are an important component of these technologies (Flagan and Seinfeld, 1988). Although these technologies have been tested in large pilot plants, they have not been commercialized.

d. Absorption processes

In these processes, solvents are used to scrub NO from flue gas. Chemical reaction is required to absorb NO in aqueous solution. Those chemical reactions can be categorized as gas phase

oxidation, liquid phase oxidation and, chelating reduction. A number of aqueous inorganic solutions have shown high capacity for NO_2 absorption, but NO is absorbed with difficulty. Consequently, a method to oxidize NO to NO_2 or an equivalent oxidized state of nitrogen is required to substantially reduce NO_x emissions. Aqueous solutions with $NaClO_2$ as oxidizing agents have been studied to determine their effectiveness in removing NO from flue gas in alkaline media. The experimental results show that an aqueous scrubbing medium containing $NaClO_2$ quantitatively oxidizes NO to NO_3^- (Yang, 1990).

Our object is to develop a totally nonaqueous organic scrubbing system for NO removal under simulated flue gas conditions. A number of dilute nonvolatile tertiary organic hydroperoxides R_3 COOH in hexadecane (cetane) solution have been tested. The results show effective absorption of NO in the range of 1000-1500 ppm. Analysis of one of the hydroperoxide scrubbing solutions showed the product of NO absorption to be mainly alkyl nitrates RONO₂. This solution can be effectively denitrated by aqueous hydrolysis.

A successful NO_X hydroperoxide scrubbing candidate would have to fulfil the following requirements:

(1) The hydroperoxide should be tertiary (R₃COOH)

Hydroperoxides (ROOH), as a class of organic oxidizing agents, are safer (i.e., thermally more stable) than peroxides ROOR (Shelton et al., 1967; Szmant, 1989), the former have a $t_{1/2}$ of 10 hours at about 170°C, whereas the latter have $t_{1/2}$ of 10

hours at 120°C or less (Szmant, 1989).

 $t_{1/2}$ is the half life of organic hydroperoxide. It is determined from the following definition:

 $t_{1/2} = Ln 2/first$ order rate constant for disappearance of the hydroperoxide

Tertiary hydroperoxides, i.e., ones lacking any \measuredangle -hydrogen, are thermally less labile than secondary and primary analogs, being safe enough to fulfil ICC requirements for handling and transport (Szmant, 1989).

(2) The hydroperoxide should be relatively inexpensive

This is important because an efficient NO_X scrubber (>90% removal) should cost no more than \$10-15,000/ton of NO_X removed if it is expected to be economically competitive with SCR (Yang, et al., 1991).

(3) The components of the scrubber solution should not be vaporized at flue gas temperatures.

(4) The "spent" scrubbing solution should be easily denitrated and the denitrated organic material then reoxidized to hydroperoxide or used in another economically advantageous way.

With these factors in mind, we chose the following four hydroperoxides for our study: 3,6-dimethyl-3-octyl hydroperoxide (1), p-menthane hydroperoxide (2), pinane hydroperoxide (3), and cumene hydroperoxide (4). The structures of these four hydroperoxides are shown in Figure 2.

Polypropylene fibers containing hydroperoxide groups were also evaluated in this study.

Figure 2. Structures of Four Organic Hydroperoxides

$$CH_3$$

$$CH_3 - CH_2 - CH_3$$

$$O - OH \qquad CH_3$$





(2) p-menthane hydroperoxide

(mix of stereolsomeric tert. hydroperoxides)



СН₃ -С-О-ОН -С-О-ОН -С-О-ОН

(3) Pinane hydroperoxide

(mix of epimers)



2 LITERATURE REVIEW

Nitrogen-containing compounds, both inorganic and organic, play extremely important roles in the chemistry of both polluted and clean atmosphere. The removal of NO_x from flue gases has received considerable attention due to federal regulations associated with the "Clean Air Act". A good understanding of NO_x removal from flue gases has not been achieved because: a. The oxidation of NO by O_2 (Hampson and Garvin, 1978) occurs

simultaneously with other processes:

$$2NO + O_2 \longrightarrow 2NO_2$$
(6)
$$k_1^{298^{\circ}K} = 2.0*10^{-38} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$$

This third order reaction is too slow at typical ambient NO concentrations to be significant (Finlayson-Pitts, 1986).

b. Absorption and desorption operations occur simultaneously.

c. Temperature plays an important role in the reactions.

d. Required physical-chemical data is generally not available.

During the past thirty years, much data have been published in various aspects of NO_x absorption. Much of these data were compiled in order to define areas for future research.

Absorption of NO followed by Oxidation

Oxidation of NO is the most important step in the NO scrubbing process. Oxidation of NO to NO₂ is relatively slow, and thus, becomes the rate limiting step in most approaches. Further more, chemical oxidation of NO is required when its concentration is very small. The common agents include: nitric acid, ozone,

hydrogen peroxide, chlorine dioxide, chlorite, peroxyacids, etc. a. Ozone

The reaction of NO with ozone is given by following equation:

$$NO + O_3 \longrightarrow NO_2 + O_2 \tag{7}$$

The resulting nitrogen dioxide can conveniently be scrubbed in caustic solutions even at low ppm values. The mechanism of above reaction has been studied by Harcourt (1972), and Bhatia and Hall (1980). The kinetics have been investigated by Borders (1982). The major disadvantage of ozone is the large power requirement which must be available in a stand-by system (Shaw, 1976).

b. Sulfuric acid

Topol (1968) used sulfuric acid as the oxidizing agent. The reaction is represents by:

 $2 \text{ NO} + 5 \text{ H}_2 \text{SO}_4 \longrightarrow 2 \text{ NO}^+ + 2 \text{ SO}_2 + \text{H}_3 \text{O}^+ + 3 \text{ HSO}_4^-$ (8) $2 \text{ NO} + 5 \text{ H}_2 \text{SO}_4 \longrightarrow 2 \text{ NO}^+ + \text{SO}_2 + 2 \text{ H}_3 \text{O}^+ + 4 \text{ HSO}_4^-$ (9)

The equilibrium constants for reactions 8 and 9 were found to be $2*10^{50}$ kg-mole/m³ and $4*10^{12}$ kg-mole/m³, respectively. The rate of reaction 9 is second order in NO and the rate constant was found to be 0.2 m³/kg-mole.s.

c. Hydrogen peroxide

Shaw (1976) reported that hydrogen peroxide does indeed oxidize NO, but large excess quantities of H_2O_2 are required to obtain a high NO conversion. Takahashi, et al., (1979) also carried out gas phase NO oxidation using hydrogen peroxide. Nitric oxide and hydrogen peroxide were taken in the ratio of 1:13 at a

temperature great than 400° C and using 100 ppm NO. The extent of NO oxidation was greater than 95%. Absorption experiments were carried out using 101.5 mm ID stirred cell by Ladhabhoy and Sharma (1969). The reaction between NO and H_2O_2 is given by the following equation:

$$NO + H_2O_2 \longrightarrow NO_2 + H_2O$$
 (10)

Absorption of NO is accompanied by fast pseudo-first order chemical reaction. The value of reaction rate constant at 30° C was found to be $8.42*10^2$ m³/kg-mole s with an activation energy of 13,700 kcal/kg-mole (Shaw, 1976).

d. Potassium permanganate

Potassium permanganate was used for the oxidation of NO by Kann, et al., (1977). Conversion of NO exceeding 80% has been reported. Sada, et al., (1977) studied the oxidation of NO using aqueous solutions of $KMnO_4$ and aqueous solutions mixed solutions of $KMnO_4$ and Aqueous solutions mixed solutions of $KMnO_4$ and NaOH.

In the absence of NaOH, the reaction between NO and $KMnO_4$ can be represented by the following equation:

$$NO + MnO_4 \longrightarrow NO_3 + MnO_2(s)$$
(11)

Shaw (1976) also found the formation of MnO_2 and the studies indicate that unbuffered $KMnO_4$ is not a desirable scrubbing medium. Uchida, et al., (1983) showed that the product of reaction with MnO_2 has some inhibiting effect on the rate of reaction.

In the presence of NaOH, the oxidation reaction enhances the reaction between NO and $KMnO_4$. In a strong aqueous caustic solu-

tion, the reaction is given by:

NO + MnO₄⁻ + 2 OH⁻ NO₂⁻ + MnO₄⁻² + H₂O (12) Similar observation have been reported by Teramoto, et al., (1969).

e. Sodium chlorite

The absorption of NO in aqueous mixed solutions of $NaClO_2$ and NaOH has been studied by Sada, et al., (1978, 1979). Oxidation of NO with $NaClO_2$ in the presence of NaOH can be presented by:

4 NO + 3 ClO_2^- + 4 OH⁻ 4 NO₃⁻ + 3 Cl⁻ + 2 H₂O (13) The results indicated that rate constant decreases with an increase in the concentration of NaOH.

Yang (1990) reported that the products of the reaction of NO and NaClO₂ in the absence of NaOH are also Cl⁻ and NO₃⁻. Although, the ratio of NO to ClO_2^- is 1 : 1 rather than 4 : 3. f. Chlorine dioxide

A Japanese patents claim the use of chlorine dioxide for NO oxidation (Hikita, 1977). The conversion of NO was claimed to be about 90%.

g. Sodium sulfite

Shaw (1976) reported that sodium sulfite is very effective for NO₂ absorption at reasonable operating temperatures. Sufficient NO was not absorbed by sulfite.

Uchida, et al., (1983) studied NO absorption which initially increases with sodium sulfite concentration, attains a maxima when the concentration of sodium sulfite is 100 mole/m^3 and then decreases.

h. Sodium dithionite

Lahiri (1981) measured specific rates of absorption of NO in aqueous caustic solutions of sodium dithionite $(Na_2S_2O_4)$ and sodium sulfide (Na_2S) at 31° and 27°C respectively. The reaction between NO and aqueous caustic solutions of $Na_2S_2O_4$ was found to be first order with respect to NO only. The first order rate constant was found to be $2.3 \times 10^3 \text{ s}^{-1}$ at 31°C. The reaction between NO and the caustic aqueous solution of sodium sulfide was found to be zero order in Na_2S and zero order in NO. The rate was found to be $1.69 \times 10^{-4} \text{ kg-mole/m}^3$ s at $27^{\circ}C$.

i. Peracid solution

Treatment of water-soluble carboxylic acids with concentrated hydrogen peroxide generate solutions of peracids. These compounds can rapidly oxidize NO_x to their respective oxyanions, making them useful in flue gas treatment.

The reactions believed to be involved in the removal process are shown in equations 14-15 (Littlejohn and Chang, 1990).

 $RCOOOH + NO - NO_2 + RCOOH$ (14)

 $RCOOOH + 2NO_2 + H_2O \longrightarrow 2NO_3 + RCOOH + 2H^+$ (15)

j. Organic hydroperoxide

Much of the known chemistry of NO_X in the presence of ROOH is the result of the study of the photooxidative reactions of ROO• in the atmosphere, illustrated by Anderson (1983) and Finlayson-Pitts (1986).

In all but the remote troposphere, the alkylperoxy radicals formed from the alkyl radicals, react with NO. The only signifi-

cant path for the smaller radicals ($< C_4$) is oxidation of NO to NO₂ and formation of alkoxy radicals:

$$ROO \bullet + NO \longrightarrow RO \bullet + NO_2$$
(16)

Only in the past few years have techniques become available for measuring the rate constants of these reaction. Hence a wide range of alkyl radicals have not been studied, and there are considerable discrepancies in the rate constants reported in the literature. However, the sparse data available indicate that the rate constants for above reaction are not very sensitive to the nature of R. As a result, until further data become available, a value of 7.6 $* 10^{-12}$ cm³ molecule⁻¹s⁻¹ is recommended (Atkinson and Lloyd, 1984) for all alkylperoxy radicals.

Finlayson-Pitts (1986) reports that essentially all of the CH_3O_2 • reacts with NO according to equation 16. For larger alkyl radicals, another reaction channel becomes significant according to Darnall, et al., 1976. This is the addition reaction to form stable alkyl nitrates:

$$ROO \bullet + NO \longrightarrow RONO_2$$
 (17)

A possible mechanism is addition followed by isomerization:

 $ROO \cdot + NO - (ROONO) * M (RONO_2) * RO \cdot + NO_2 (18)$ M $RONO_2$

Studies of a variety of alkanes have established that the addition channel can become quite significant (>30%) for certain alkyl radicals depending on their structure and size (Atkinson,

et al., 1982).

Table 2 shows that for some simple alkyl radicals, the fraction of the overall reaction of ROO• with NO results in alkyl nitrate formation at atmospheric pressure, that is, the ratio $k_{17}/(k_{16} + k_{17})$. The increasing importance of addition as the R group increases in size reflects the longer lifetimes of the larger excited intermediates, which allows more vibrational modes before collisional deactivation to the stable nitrate as opposed to its decomposition. As expected, the observed alkyl nitrates from straight chain alkanes which correspond generally to abstraction of a secondary hydrogen atoms rather than that of a stronger primary hydrogen. Somewhat surprisingly, the rate constant ratio $k_{17}/(k_{16} + k_{17})$ is smaller for tertiary alkylperoxy radicals; the reasons for this are unclear (Atkinson, et al., 1984).

Alkylperoxy radicals also react rapidly with NO₂, but the nitrates formed thermally decompose back to the reactants:

$$ROO \bullet + NO_2 \longrightarrow ROONO_2$$
 (19)

Thus no over all reaction occurs, and this process acts primarily as a low-temperature storage for NO_2 (Finlayson-Pitts, 1986).

In one of the first of a small number of studies of ROOH-NO reactions in the condensed phase, Shelton and Kapczewski (1967) reported that reaction of 100% NO with a dilute solution of tbutyl hydroperoxide in benzene afforded t-butyl nitrate and tbutyl nitrite via a 4-step NO-induced free radical reaction sequence, shown in equations 20-23:

	Primary		Secondary		Tertiary	
Alkane	RO ₂	$k_{17}/(k_{16} + k_{17})$	RO ₂	$k_{17}/(k_{16} + k_{17})$	RO ₂	$k_{17}/(k_{16} + k_{17})$
Ethane	Ethyl	≤0.014				
Propane	1-Propyl	0.020	2-Propyl	0.042		
<i>n</i> -Butane	I-Butyl	≼0.041	2-Butyl	0.090		
<i>n</i> -Pentane			2-Pentyl	0.129, 0.134		
			3-Pentyl	0.131, 0.146		
Neopentane	Neopentvl	0.051				
2-Methylbutane			2-Methyl-3-butyl	0.141	2-Methyl-2-butyl	0.047
<i>n</i> -Hexane			2-Hexyl	0.209		
			3-Hexyl	0.230		
Cyclohexane			Cyclohexyl	0.160		
2-Methylpentane			2-Methyl-3-pentyl	0.190	2-Methyl-2-pentyl	0.031
			+2-Methyl-4-penty	1		
3-Methylpentane			3-Methyl-2-pentyl	0.178		
n-Heptane			2-Heptyl	0.301, 0.291		
			3-Heptyl	0.323, 0.325		
			4-Heptyl	0.301, 0.285		
n-Octane			2-Octyl	0.323		
			3-Octyl	0.348		
			4-Octyl	0.329		

.

Table 2. Fraction of Reaction of RO₂ + NO Producing Alkyl Nitrates for Individual Alkylperoxy Radicals at Room Temperature and 735-740 Torr Total Pressure

Source: Carter and Atkinson, 1985.

t-BuOOH + NO	$-$ t-BuO \cdot + HONO	(20)
--------------	--------------------------	------

 $t-BuO \cdot + t-BuOOH \longrightarrow t-BuOH + t-BuOO \cdot$ (21)

 $t-BuOO \cdot + NO - [t-BuOONO] - t-BuONO_2$ (22)

t-BuOH + HONO - t-BuONO + HOH (23)

These reactions were certainly not run under typical flue gas conditions, i.e., elevated temperature and dilute NO_x stream (not to mention the presence of other gases such as CO_2 , SO_2 , NO_2 and O_2 , etc.).

Carlsson, et al., (1988) repeated that concentrated hydroperoxide compounds react with 100% NO to give alkyl nitrate as the dominant products with only trace amounts (< 5%) of alkyl nitrites. Rather than the NO-induced O-O scission (equation 20) proposed by Shelton and Kapczewski (1967), Carlsson, et al., (1988) proposed that the hydrogen was abstracted by NO (reaction 24-25). A similar scheme may explain nitrite formation from alcohols.

$$R_3 COOH + NO \longrightarrow R_3 COO \cdot + HNO$$
 (24)

$$R_3 COO \bullet + NO \longrightarrow [R_3 COONO]^* \longrightarrow R_3 CONO_2$$
(25)

In these experiments, a green yellow gas was observed, that could possibly have been HNO.

These results, like Shelton and Kapczewski's experiments, were not run under typical flue gas conditions. Furthermore, the presence of concentrated ROOH solutions would be economically unacceptable in a flue gas scrubber.

Smallwood (1929) found that nitric oxide was a catalyst for hydrogen-atom removal without itself being consumed (over 99% of

the NO was recovered). He proposed nitroxyl, HNO, as an intermediate to hydrogen-atom recombination. Further evidence for HNO as an intermediate was provide by Harteck (1933). More recently, Taylor and Tanford (1944), as well as Hoffman and Benstein (1960), studied the mercury-sensitized decomposition of hydrogen in the presence of nitric oxide, and they too, postulated HNO as an intermediate.

The most quantitative work on HNO was done by Clyne and Thrush (1961, 1962). In their classic studies, they passed an electric discharge through hydrogen in a flow tube, added NO past the discharge, and monitored the chemiluminescence at various points downstream. They deduced the mechanism shown in equations 26-30:

$$H \cdot + NO + M \longrightarrow HNO + M$$
 (nonradiative) (26)

$$H \cdot + NO + M \longrightarrow HNO^{*}(^{1}A'') + M$$
 (27)

 $HNO^* \longrightarrow HNO(^1A') + hv$ (28)

$$HNO^* + M \longrightarrow HNO + M$$
 (29)

$$H \cdot + HNO \longrightarrow H_2 + NO$$
 (30)

In this mechanism $HNO^*({}^1A")$ and $HNO^*({}^1A")$ represent different vibration levels of HNO^* intermediates which are vibrationally excited, M is a third body (Noyes, et al., 1968).

3 EXPERIMENTAL

Details of the laboratory apparatus, chemicals and gases used to conduct the experiments of this thesis are described in this section.

3.1 Materials

3.1.1 Organic hydroperoxides

a. 3,6-dimethyl-3-octyl hydroperoxide (1)

The compound 3,6-dimethyl-3-octyl hydroperoxide (1) was prepared in our laboratory by Mr. Charles Wenger (1990) using standard method reported by Foreman, et al., 1957 and Gilmont, et al., (1962). To a vigorously stirred mixture of 870 grams of 85% H_3PO_4 and 516 grams of 50% H_2O_2 , was added 300 grams of 3,6-dimetyl-3octanol over 30 minutes. The reactant mixture was stirred at $44^{\circ}C$ for three days. The upper organic layer was dissolved in 525 ml of ethyl ether. The ether solution was washed with water, followed by 5% NaHCO₃ and water, and dried over anhydrous MgSO₄. The dried ether solution was 3,6-dimethy-3-octyl hydroperoxide. This material was used without further purification.

b. Commercial hydroperoxides

Three commercial tertiary hydroperoxides, p-menthane hydroperoxide (2), pinane hydroperoxide (3), and cumene hydroperoxide (4) were obtained from Atochem North America, SCN/Glidco, and Aldrich Chemical Co., respectively, and were used without further purification.

The purities of these organic hydroperoxides were analyzed by

Wenger (1990) using iodometric titration. Hydroperoxides, being strong oxidizing agents, are generally diluted with inert materials in order to assure safety during shipment. Iodometric methods are commercially used for determining the concentration of organic hydroperoxides. The iodide ion reacts stoichiometrically with hydroperoxides in acidic solution, producing iodine, which can be titrated with thiosulfate or estimated colorimetrically (Swern, 1972). The chemical and physical properties of these four compounds are listed in Table 3. Different concentrations of these hydroperoxides were prepared by mixing them with n-hexadecane solvent.

3.1.2 Gases

The nitric oxide feed mixtures in helium were purchased from Liquid Carbonic Co. and used directly from cylinders. Different concentrations of NO were obtained by diluting the mixture with pure helium. The purity of NO in the mixed gases was reported to be 99.99% by the supplier.

The 99.99 percent pure helium cylinders were also supplied by Liquid Carbonic Co..

3.1.3 Isobutyl nitrate and tertbutyl nitrite standards for infrared calibration

In order to estimate the distribution of product nitrates and nitrites in the organic and conduct a nitrogen material balance, isobutyl nitrate and tertbutyl nitrite were used as IR standards. This was done by matching the characteristic RONO and RONO₂ infrared (IR) absorption bands of standard concentrations of
Table 3. Analytical and Physical Data for Hydroperoxides

Hydroperoxide	Cost/lb	t1/2 at 120°C ª	Purity,%	B.P.°C ^b	Company
3,6-dimethyi-3-octyi hydroperoxide			95	200	made in our Iaboratory
P-Methane hydroperoxide	\$2	> 50h	56	200	Elf-Aquitaine
Pinan o hydroperoxide	\$ 1.5	100 h	42	180	glidco
Cumene hydroperoxide	\$ 0.8	> 500h	70	200	ALDRICH

a : obtained from Szmant (1989)

b : obtained from manufacturer

of these compounds with the same bands from spent scrubbing solutions. Different concentrations of isobutyl nitrate and tertiary butyl nitrite solutions were prepared by mixing them with hexadecane solvent. The purity of purchased isobutyl nitrate and tertiary butyl nitrite were reported by the supplier Aldrich Chemical Company, to be 99% and 90%, respectively. They were used without further purification.

3.1.4 Hexadecane solvent

The 99% pure n-hexadecane (cetane) solvent was purchased from Aldrich Chemical Company and used without further purification.

3.2 Apparatus

The experiments were conducted in a laboratory-scale scrubber reactor system show in Figure 3. The basic scrubbing apparatus consists of a 56 cm long glass pipe 2.54 cm in diameter as the scrubber reactor. The flow rates of inlet gases were measured with two calibrated Cole Parmer rotameters. Heating tape was used to vary the reactor temperature. The reactor temperature was monitored by a Chromel-Alumel thermocouple inserted between reactor and heating type. To avoid the organic vapor condensing in the analytical system, an a glass U-tube immersed in ice water was used as a condenser.

3.3 Experimental Procedure for Scrubbing

A premeasured volume of organic hydroperoxide solution was place in the reactor. Pure helium gas was introduced into the bottom of the reactor through a fritted glass disk by turning a three point value to allow helium to purge the flow system in

Figure 3. Flow Schematic of NO Absorption Unit



order to remove air from the filling operation. After purging, the reactor was heated to the desired temperature while maintainthe He flow, and the three point valve was turned to allow ing the desired concentration of nitric oxide gas to enter the scrub-Part of the effluent gas was first passed through an iceber. bath to condense the organic vapor and then analyzed either by an line GOWMAC gas chromatograph with a thermal conductivity on detector, or by a chemiluminescent NO, analyzer (ThermoElectron Corp). The feed concentration was checked penodically during the experiment by by-passing the reactor. The remainder of the effluent gas was discharged into a hood. Small samples of the scrubbing solutions were collected during the experiment for later analysis with a Fourier Transform-Infrared Spectrometer (FTIR).

3.4 Experimental Procedure for Denitration

Two mL of a scrubbing solution of 0.49 M p-menthane hydroperoxide in cetane which had taken up NO was mixed with 20 mL of 10% aqueous ammonia. The resulting heterogeneous mixture was vigorously stirred magnetically at 70°C for 12 hours. The mixture was allowed to cool to room temperature. The upper organic layer was dried over anhydrous granular Na_2SO_4 and taken for FTIR analysis. The lower layer was taken for ion chromatography (IC) analysis (Barlettano, 1991).

3.5 Analytical Technique

3.5.1 Gas chromatograph (GC)

The outlet line carrying the scrubber effluent gas entered an on line GOWMAC gas chromatograph with thermal conductivity detec-

tor (TCD) for measurement of the concentration of NO. The column used was a 1/8 inch in diameter by 6 feet long stainless steel column packed with 80/100 mesh 5A Molecular Sieve. A Hewlett Packard 3396 integrator was used as both recorder and integrator. Figure 4 shows typical peak resolution and retention time for nitric oxide.

GC operating conditions:

Oven temperature = $150^{\circ}C$ Detector temperature = $180^{\circ}C$ Injection port temperature = $160^{\circ}C$ Detector current = 200 mACarrier gas flow rate = 30 ml/minReference gas flow rate = 30 ml/min

Figure 5 shows the peak-area concentration calibration curve for NO. Using this curve, inlet and outlet concentrations of NO can be calculated.

3.5.2 Chemiluminescent NO_x analyzer

A ThermoElectron NO_x analyzer was used to measure the concentration of NO and NO_2 . This instrument makes use of the chemiluminescent properties of the NO reaction with ozone as a measure of NO concentration. NO molecules are mixed with O_3 from the ozone generator and carried into a reaction chamber where NO is electronically converted to excited NO_2 . Excited NO_2 then emits light (chemiluminescence).

$$NO + O_3 - NO_2^* + O_2$$
 (31)

$$NO_2^* \longrightarrow NO_2 + hv$$
 (32)

Figure 4. Gas Chromatoghaph Peak Resolution

.



MUL FACTOR=1.0000E+00





Balance gas : Helium

The basic chemiluminescent analyzer is only sensitive to NO molecules. NO₂ is measured by thermally converting the NO₂ to NO and measuring the incremental increase in concentration of NO. 3.5.3 Fourier transform-infrared spectrometer (FTIR)

The Fourier transform-infrared spectrometer is used for qualitative and quantitative analysis of organic nitrates and nitrites in the scrubbing solutions. The basis of any FTIR spectrometer is the Michelson interferometer. IR theory states that a molecule may absorb infrared radiation of the appropriate frequency to excite it from one vibrational or rotational state to another. When a beam of infrared energy, covering a broad frequency range, is passed through a sample, the energy at certain frequencies is absorbed by the sample. A graph of energy absorbed versus frequency is the absorption spectrum of the sample. The spectrum is characteristic of the particular molecule and its molecular motions. Typical FTIR spectra for isobutyl nitrate and tertiary butyl nitrite are shown in Figures 6 and 7, respectively.

3.5.4 Ion chromatograph (IC)

A Waters ion chromatograph and associated equipment were used to measure the concentration of NO_3^- and NO_2^- ions in aqueous solutions.

In this system, the sample injection is pushed by buffer eluent through the analytical column, where ions are separated. After separation, the sample is carried to a conductivity detector, which is based upon the electrical conductivity of the



Figure 6. FTIR Spectrum of Isobutyl Nitrate Standard



sample when placed between two oppositely charged electrodes. The presence of ions in the solution allows electrical current to flow between the electrodes, completing the circuit. At low concentrations, conductivity is directly proportional to the concentration of ions in solution. A typical chromatogram is given in Figure 8.





ω 5

4 RESULTS AND DISCUSSION

A number of dilute solutions of tertiary organic hydroperoxides were tested as NO oxidizing agents. The effects of temperature, hydroperoxide concentration, NO concentration in the gas feed, and gas flow rate on removal of NO were evaluated.

The objectives of this study are to:

- * Evaluate the potential of organic hydroperoxides to oxidize and absorb NO.
- * Determine optimum conditions for NO oxidation.
- * Identify all effluent products.
- * Postulate possible reaction mechanisms.
- * Calculate the nitrogen balance

The oxidizing and adsorbing/desorbing ability of hydroperoxylated polypropylene fibers were also studied.

4.1 Effect of Operating Parameters on NO Removal

4.1.1 NO conversion as a function of reaction time

The relationship between NO oxidation and time as a function of organic hydroperoxides was determined. Figures 9, 10, and 11 show the experimental results for 0.3 M p-menthane hydroperoxide and two concentrations, 0.23 M and 0.51 M, pinane hydroperoxide, respectively. At the beginning of each experiment, no NO oxidation is observed, then conversion increases rapidly, reaching a steady state in less than 1 hour. The time required to reach steady state seems to be a function of hydroperoxide concentration. Higher hydroperoxide concentrations require less time to

Figure 9. NO Conversion, vs., Time at 90 °C with 0.296 M p-Menthane Hydroperoxide



NO inlet concentration = 1500 ppm Gas flow rate = 1000 cc/min Solution volume = 200 cc

Figure 10. NO Conversion, vs., Time at 90 °C with 0.230 M Pinane Hydroperoxide

ł



NO inlet concentration = 1500 ppm Gas flow rate = 1000 cc/min Solution volume = 200 cc

Figure 11. NO Conversion, vs., Time at 90 ^o C with 0.505 M Pinane Hydroperoxide



NO inlet concentration - 1500 ppm Gas flow rate - 1000 cc/min Solution volume - 200 cc

reach steady state. Conversion of NO remains constant until breakthrough.

4.1.2 Effect of temperature on NO oxidation

A number of experiments were carried out to test the oxidation of NO in 0.3 M p-menthane hydroperoxide and 0.3 M pinane hydroperoxide as a function of temperature. These experiments were conducted with 1500 ppm NO in helium flowing at 1000 cc/min into 200 cc of solutions.

Results shown in Table 4 indicate that NO can be oxidized by both hydroperoxides, and higher conversion of NO are achieved with increasing temperature.

Another set of runs was made at the same conditions as indicated above to evaluate the effect of temperature as well as residence time on NO oxidation with cumene hydroperoxide, 3,6dimethyl-3-octyl hydroperoxide, and pinane hydroperoxide. In these runs, the flow rates were reduced to 150 cc/min. It should be noted that the pinane hydroperoxide run was made with 1100 ppm in helium rather than 1500 ppm because the latter gas mixture was consumed. However, the effect of this small change in NO concentration was insignificant (see Figure 13, p. 46).

The results for this set of runs are also summarized in Table 4. The results indicate that increasing the residence time significantly increases the rate of oxidation of NO. Temperature also plays an important role in NO removal, elevated temperatures favor NO oxidation. It should be pointed out that above 90°C, 3,6-dimethyl-3-octyl hydroperoxide decomposes, thus decreasing

Table 4. Effect of Temperature on NO Scrubbing

with Organic Hydroperoxides

Organic hydroperoxides	Concentration, M	Temperature, ⁰ C	Gas flow rate, cc/min	Conversion, %
4 - 27 - 27 - 27 - 27 - 27 - 27 - 27 - 2	0.300	25	150 ⁸	0
3,6-dimethyl-3-octyl	0.300	50	150 ⁸	45.8
hydroperoxide (1)	0.300	0.300 70 150		81.6
	0.300	90	150 ⁸	67.7
	0.296	25	1000 ⁸	0
	0.296	50	1000 ⁸	9.4
p-Menthane	0.296	80	1000 ⁸	32.2
hydroperoxide (2)	0.296	90	1000 ^a	49.7
	0.306	25	150 b	0
	0.306	50	150 b	26.3
Pinane	0.306	70	150 b	97.4
hydroperoxide (3)	0.306	90	150 b	100

Table 4. Effect of Temperature on NO Scrubbing

with Organic Hydroperoxides (continued)

Organic hydroperoxides	Concentration, M	Temperature, ^O C	Gas flow rate, cc/min	Conversion, %
	0.306	25	1000 ⁸	0
Pinane	0.306	55	1000 ⁸	22.2
hydroperoxide (3)	0.306	65	1000 ⁸	31.7
	0.306	80	1000 ^a	61.9
	0.306	90	1000 ^a	79.4
	0.303	25	150 ⁸	0
Cumene	0.303	50	150 ⁸	27.7
hydroperoxide (4)	0.303	70	150 ⁸	80.6
	0.303	90	150 ⁸	100

Solution volume = 200 cc

a : NO inlet concentration = 1500 ppm

b : NO inlet concentration = 1100 ppm

the NO conversion rate.

4.1.3 Effect of tertiary organic hydroperoxide concentrations in hexadecane on NO oxidation

A series of experiments using the hydroperoxide compounds as oxidizers for NO in the gas feed was conducted to determine the effect of concentrations on NO oxidation. The effectiveness of pinane hydroperoxide was evaluated over the range 0.2 M to 0.5 M at 90° C with 1500 ppm NO. Cumene hydroperoxide was similarly evaluated over the 0.1 M to 0.5 M range, but with 1100 ppm NO. In both cases the scrubber contained 200 cc of solution and the gas flow rate was 1000 cc/min.

The experiment results are summarized in Table 5 and Figure 12. Figure 12 clearly indicates that higher concentrations of the hydroperoxides improve the oxidation of NO. Figure 13 shows that the effect of cumene hydroperoxide on 1100 ppm NO is essentially indistinguishable from its effect on 1500 ppm NO.

4.1.4 Effect of gas flow rates on NO oxidation

Experiments were conducted to determine the effect of residence time on NO oxidation with 0.3 M 3,6-dimethyl-3-octyl hydroperoxide and 0.3 M cumene hydroperoxide at same inlet NO feed concentration of 1500 ppm, 90°C reaction temperature and 200 cc scrubbing solution volume. The gas flow rates used were 150 cc/min and 1000 cc/min, which correspond to residence times in the scrubber of 80 seconds and 12 seconds, respectively.

The results are shown in Table 6. At high flow rates, or low residence times, the rate of NO oxidation significantly de-

Table 5. Effect of Organic HydroperoxideConcentrationon NO Scrubbing

Organic hydroperoxides	Concentration, M	Temperature, ^O C	NO inlet conc., ppm	Conversion, %
Pinane	0.230	80	1500	55.2
hydroperoxide (3)	0.306	90	1500	79.4
	0.505	90	1500	97.2
	0.101	90	1100	51.8
Cumene	0.199	90	1100	80.0
hydroperoxide (4)	0.303	90	1100	89.9
	0.506	90	1100	95.7

Gas flow rate = 1000 cc/min

Solution volume = 200 cc

Figure 12. Conversion of NO in Organic Media



• Pinane O Cumene

Feed = 1500 ppm NO in **Hellum** Temperature = 90 ^OC Solvent = Cetane

Figure 13. Cumene Hydroperoxide Concentration, vs., NO Conversion



Gas flow rate = $1000 \ cc/min$ Solution volume = $200 \ cc$ Operating temperature = $90^{\circ}C$

Table 6. Effect of Gas Flow Rate on NO Scrubbingwith Organic Hydroperoxides

Concentration, M	Flow rate, cc/min	NO inlet conc., ppm	Conversion, %
0.300	150	1500	67.6
0.300	1000	1500	44.6
0.306	150	1100	100
0.306	1000	1500	79.4
0.303	150	1500	100
0.303	1000	1500	84.2
	Concentration, M 0.300 0.300 0.306 0.306 0.306 0.303 0.303	Concentration, M Flow rate, cc/min 0.300 150 0.300 1000 0.306 150 0.306 150 0.306 150 0.303 150 0.303 150 0.303 1000	Concentration, M Flow rate, cc/min NO inlet conc., ppm 0.300 150 1500 0.300 1000 1500 0.306 150 1100 0.306 1500 1500 0.306 1500 1500 0.303 1500 1500

Operating temperature = 90°C

Solution volume = 200 cc

creases.

Similar results were obtained when pinane hydroperoxide was used as the oxidizer at the same two gas flow rates. In these experiments the gas feed contained either 1100 or 1500 ppm NO as indicated in Table 6.

4.1.5 Color change in the reaction

Color changes were observed throughout the experiments with all four hydroperoxides. During first few hours of the reaction, the solution color changed from colorless to green then gradually became yellow. The green color may be due to the formation of a reasonably high concentration of HNO intermediate (Carlsson, et al., 1988, see p. 20).

According to the results described above, the effects of temperature, gas flow rate, and hydroperoxide concentration on NO oxidation for all four organic hydroperoxides are similar. Higher conversions of NO can be achieved at higher temperatures, higher concentrations of organic hydroperoxides and higher residence times (lower gas flow rates). These results are consistent with reaction rate theory, where temperature, reactant concentration and residence time increase the quantity of NO reacted.

The result also show that pinane hydroperoxide and cumene hydroperoxide can remove NO more effectively than 3,6-dimetyl-3octyl hydroperoxide and p-menthane hydroperoxide. Further study is required to explain the differences in reactivity. Table 7 compares the NO-removing ability of the four organic hydroperoxides at similar operating conditions.

Table 7.	NO-removir	g Ability	of Hydrope	eroxides
----------	------------	-----------	------------	----------

	Concentration, M	Conversion, %
3,6-dimethyl-3-octyl hydroperoxide	0.300	44.6
p-menthane hydroperoxide	0.296	49.7
Pinane hydroperoxide	0.306	79.4
Cumene hydroperoxide	0.303	84.2

NO inlet concentration = 1500 ppm

Gas flow rate = 1000 cc/min

Operating temperature - 90 °C

Solution volume - 200 cc

4.2 Product Analysis

Four different analytic techniques were used to determine the final products. During the initial phases of this research, it was assumed that the hydroperoxides would oxidize NO to NO2. A gas chromatograph with thermal conductivity detector was used to qualitatively analyze for NO_2 . A standard NO_x gas mixture which contained 659 ppm NO and 224 ppm NO₂ was used as a standard. Our effort to analyze for NO2 failed, because a GC column that would separate NO₂ was not found. Consequently, a chemiluminescent NO_x analyzer was then connected to the effluent from the scrubbing reactor to directly determine if NO2 is formed. The results were not conclusive because a small amount of organic vapor which was not condensed in the ice-bath entered the $\mathrm{NO}_{\mathbf{X}}$ analyzer and interfered with the analysis. Finally, an ion chromatograph was used to analyze the aqueous solution which was used to scrub the gaseous effluent from the organic scrubber. In this experiment, a blank solution was first collected by bubbling the initial NO gas stream through a distilled water scrubber, after removing dissolved air by bubbling helium though the water. Then a normal scrubbing experiment was conducted in which a distilled water scrubber followed the usual p-menthane hydroperoxide solution scrubber. Both water samples were tested by ion chromatography. The IC results shown that the same amount of NO_3^- was present in the scrubbing solution effluent and the blank (see Figures 14, 15 and 16) (The existence of chlorine ion in both solutions may due to a water the contamination). These experiments proved that no

Figure 14. Ion Chromatogram of Blank Water Sample



Scrubbing time = 5 hours





First scrubber contained: Menthane hydroperoxide concentration = 0.103 M Operating temperature = $80^{\circ}C$ Operating time = 5 hours

Figure 16. Ion Chromatogram from Aqueous Scrubbing Solution



Menthane hydroperoxide concentration = 0.276 MOperating temperature = $80^{\circ}C$ Operating time = 5 hours NO₂ was produced in these experiments. Thus the shown in reaction equation 16 is ruled out (see literature review section, p. 17).

The analytical technique used for measuring changes in composition of the organic scrubbing solution is Fourier transforminfrared spectroscopy (FTIR). Standard solutions of isobutyl nitrate and tertiary butyl nitrite were used to calibrate the instrument. We assumed that these lower molecular weight nitrate and nitrite peaks respond quantitatively in the same way as the nitrates and nitrites produced from the tertiary hydroperoxides. The calibration curves for both isobutyl nitrate and tertiary butyl nitrite are shown in Figures 17 and 18. The final scrubbing solution from p-menthane hydroperoxide scrubbing experiments was tested for nitrogen compounds. The FTIR spectra from isobutyl ni-trate and tertiary butyl nitrite contain many bands in the region between 1700 cm^{-1} to 700 cm^{-1} that are useful for product identification. Major bands and their absorbance peaks location are listed in Table 8 (Carlsson, et al., 1986). Before testing the used scrubbing solution, a sample of the starting solution containing p-menthane hydroperoxide in hexadecane was analyzed in order to subtract its spectrum from the product spectrum. The FTIR spectra from pure hexadecane, the starting organic solution, and the final scrubbing solution are shown in Figures 19, 20, and 21. After subtraction, the absorbance peak at 780 cm⁻¹ which is characteristic of nitrite disappeared. The absorbance peak at 1630 cm⁻¹ which represents both nitrate and nitrite bands and the absorbance peak at 1290 cm^{-1}

Figure 17. Isobutyl Nitrate Infrared Calibration Curve



Absorbant intensity at wavenumber 1630 cm⁻¹

0.20 mm cell

ភូភូ

Figure 18. Tertiary Butyl Nitrite Infrared Calibration Curve



0.20 mm cell

5 ნ

Group	Model compound*	Absorbance maximum (cm ⁻¹) [Extinction coefficient, litre mole ⁻¹ cm ⁻¹]			
H CONO, H	CH ₃ (CH ₂) ₁₀ ONO ₂	642 [2 200]	1 279 [1 210]	860 [421]	
––C––ONO2 –– H	2,6,8—(CH3)3—4-nonyl nitrute	633 [1 933]	1 277 [660]	867 [544]	
- CONO2	tertbutyl nitrate	1 630 [422]	1 300 [260]	860 [140]	
	1,1,3,3-tetramethyl-1-butyl nitrate	1 628 [420]	1 292 [408]	865 [140]	
H H 	CH3(CH3)3ONO	1 657 [470]			780 [245]
I C ONO I H	2,6,8	648 [798]			778 [6.19]
 C ONO 	tert-butyl nitrite	1 638 (780)			760 [652]
Ovidi-ud autom					
Oxidized LLDP	E	63 645 (wk)	1 276	870	778 (wk)
Oxidized LLDP	E after iddometry	1 645 1 657 (mk)			778
Oxidized iPP		1 629	1 302 (sh) 1 290 1 278 (sh)	865	760 (wk) 778 (wk)
Dxidised iPP aft	er iodometry	l 638 l 646 (sh) l 653			760 778

Table 8. IR Data for Model Nitrates and Nitrite

" As dilute solutions in hexane.

* Abbreviations: wk-weak; sh-shoulder.



Figure 19. FTIR Spectra of Fresh Solution and Solvent

* Initial solution: 0.173 M menthane hydroperoxide solution ** Solvent: hexadecane

58 С






Figure 21. Comparison of FTIR Spectra from Fresh and

which represents nitrate are still present (see Figure 22). That means that only organic nitrates were produced in this experiment.



These results can be explained using the reaction mechanisms described in the literature review section (pp. 17-21). Lack of a gaseous NO_2 product rules out reaction 16. Lack of a RONO product rules out reactions 20 to 23. In other words, the most likely reaction sequence follows equations 24 and 25 (see pp. 17-20).

4.3 Nitrogen Balance

The definition and calculation of the nitrogen material balance in these experiments with p-menthane hydroperoxide as the NO oxidizer are described in this section.

4.3.1 Definition of nitrogen balance

The nitrogen balance throughout the experiment is defined as follow:

nitrogen balance = $\frac{(N_1 + N_g)_{out}}{N_{in}}$ * 100% Where:

> (N₁)_{out} represents the moles of organic nitrate in the spent scrubbing solution.

 $(N_g)_{out}$ represents the total number of moles of NO that

Figure 22. Composite Spectrum Consisting of the Difference Between the Starting and Final Solution Spectrum



left in the effluent gas.

N_{in} represents the total number of moles of NO that were bubbled through the solution

4.3.2 Calculation of nitrogen balance

To calculate the nitrogen balance, the following data were used:

Gas steam:

NO concentration = 1,500 ppm

Flow rate = 1,000 cc/min

Solution:

Concentration of p-menthane hydroperoxide (2) = 0.296 M Volume = 200 cc Temperature = $90^{\circ}C$

The amount of inlet NO is calculated according to following equation:

Where :

conc. of NO = 0.15 %
flow rate = 1,000 cc/min
t = time in minutes that NO is bubbled through the
solution.

$$V = \frac{298 \text{ K}}{273 \text{ K}} * 22,400 \text{ cc/mol} = 24,500 \text{ cc/mol}$$

Thus :

$$NO_{in} = \frac{0.15\% * t (min) * 1000 (cc/min)}{24500 (cc/mol)}$$
$$= 6.12 * 10^{-5} * t (mol)$$

The amount of NO in the outlet gas phase is estimated from the degree of conversion at a certain reaction time. The conversion data as a function of time are shown in Table 9. From this table, the conversion of NO at certain reaction time can be calculate using following equation:

 $(NO)_{out} = NO_{in} * (1 - conversion)$

The amount of NO in the effuent gas at different reaction time is listed in Table 10.

As described earlier, only organic nitrate was formed in the reaction with p-menthane hydroperoxide. To calculate the amount of p-menthane nitrate formed, different concentrations of standard isobutyl nitrate solutions were measured and calibrated using FTIR spectrometer. The concentration of nitrate as a function of absorbance intensity calibration curve is show in Figure 16. The concentrations of p-menthane nitrate in effluent solutions can be read from Figure 17 by measuring their absorbance intensities. The absorbance intensities of p-menthane nitrate at different reaction times are shown in Table 9. Thus, the moles of p-menthane nitrate in the effluent solutions at different reaction time can be calculated as follow:

moles of p-menthane nitrate = C_n (M/L) * 0.2 (L)

Where:

 C_n represents the concentration of p-methane nitrate.

Scrubbing time , hours	Conversion, %	Absorbance intensity	
4.0	50.1	0.263	
4.5	48.0	0.279	
5.0	47.7	0.287	
5.5	50.3	0.292	
6.0	50.5	0.308	
6.5	50.6	0.326	
7.0	50.2	0.351	
7.5	50.5	0.363	

Table 9. Raw Data for Calculation of Nitrogen Balance

Table 10. Nitrogen Balance

Scrubbing Time Houre	Total NO in Moles	Conversion %	Total NO out Moles	Total menthane nitrate Moles	Balance %
4.0	1.47•10^-2	50.1	7.34•10 ^-3	8.06+10^-3	104.6
4.5	1.72•10^-2	48.0	8.93•10^-3	9.19•10 [~] -3	105.4
5.0	1.84•10*-2	47.7	9.62•10*-3	9.44•10*~3	103.4
5.5	2.03 • 10 2	50.3	1.01•10*-2	9.76 - 10 ^ - 3	98.1
6.0	2.21•10*-2	50.5	1.09•10*-2	1.02•10*-2	95.7
6.5	2.39•10^-2	50.6	1.18•10*-2	1.07 • 10 ^ - 2	94.1
7.0	2.58•10^-2	50.2	1.28•10*-2	1.17•10^-2	95.3
7.5	2.76+10*-2	50.5	1.37•10*-2	1.23 • 10 * - 2	94.2

Total NO out - total NO in • (1 - conversion) Balance - (total menthane nitrate + total NO out) / total NO in • 100% Menthane hydroperoxide concentration - 0.296 M Temperature - 90 °C Flow rate - 1000 cc/min NO concentration - 1500 ppm 0.2 L is the volume of organic solution. The results are shown in Table 10.

According to the definition of nitrogen balance, the nitrogen balance at different reaction times was calculated and is listed in Table 10. The results show that the mole ratio of NO reacted to RONO₂ produced being 1:1.

Also, as described earlier, the solution color changed from colorless to green and then became yellow during the reaction, which is consistent with the formation of HNO as a intermediate product during the experiment. All these results are consistent with the results of Carlsson, et al., (1988) who found that condensed phase reactions of concentrated alkyl hydroperoxides with 100% NO afforded only alkyl nitrate. Thus, a possible reaction mechanism of our experiment with p-menthane hydroperoxide as reactant can be written as follow:

$$R_3 COOH + NO \longrightarrow R_3 COO \cdot + HNO$$
 (33)

$$R_3 COO \cdot + NO \longrightarrow [R_3 COONO] \longrightarrow R_3 CONO_2$$
 (34)

$$R_3 COOH + HNO \longrightarrow R_3 COO \cdot + H_2 + NO$$
(35)

One way of confirming the likelyhood of this mechanism is to analyze for the production of hydrogen. Alternatively, one could postulate the following reaction:

 $HNO + HNO - H_2O + N_2O$ (36)

This could be confirmed by looking for water and nitrous oxide in the gas phase.

4.4 Denitration Studies

Since organic nitrates such as R₃CONO₂ are structurally

similar to the nitrocellulose and nitroglycerine used to make military explosives, we explored the application of known methods to denitrate nitrocellulose to the products from NO absorption. There have been reports of chemical (Bluhm, 1976) and biological (Dogliotti, et al., 1974) denitration of these materials. However, the most promising process for the present application is the use of dilute aqueous ammonia which can quantitatively denitrate nitrocellulose to pure cellulose and ammonium nitrate, the latter compound being a fertilizer (Equation 37).

 $cell-(ONO_2)_3 + NH_4OH \longrightarrow cell-(OH)_3 + NH_4^+NO_3^-$ (37)

We decided to attempt the denitration of p-menthane nitrate using the above method (See experimental procedure on page 27).

The characteristic 1630 $\text{cm}^{-1} \text{ RONO}_2$ band present in the initial solution showed a dramatic decrease in intensity. From a comparison of the relative peak areas of the 1630 cm^{-1} (RONO₂) to 1500 cm^{-1} (-CH₂-) bands in the organic solution before and after ammonia treatment it was estimated that 85% of the organic nitrate had been hydrolyzed. Ion chromatographic analysis of the aqueous layer showed the presence of NO₃⁻, thus confirming the hydrolysis of p-menthane nitrate (Barlettano, 1991).

5 CONCLUSIONS

A series of experiments were performed in order to evaluate the ability of tertiary organic hydroperoxide solutions to remove NO from a gas stream. Four organic hydroperoxides were evaluated in these experiments. In section 7, some experiments using hydroperoxylated polypropylene fibers to remove NO are described. The conclusion from this research are listed below:

1. Cumene hydroperoxide and pinane hydroperoxide are the best oxidizers out of the four organic hydroperoxides tested with NO containing gas streams (see Table 7).

2. Quantitative removal of 1500 ppm NO is obtained at $90^{\circ}C$, 150 cc/min gas flow rate, with both 0.303 M cumene hydroperoxide and 0.303 M pinane hydroperoxide.

3. Rate of NO removal increases with temperature, hydroperoxide concentration, and residence time.

4. Nitrogen material balances were calculated to within $100 \pm 10\%$ with p-menthane hydroperoxide as the absorber. The material balance is based on p-menthane nitrate being the only nitrogen containing product.

5. The p-menthane nitrate can be efficiently denitrated in dilute aqueous ammonia.

6. The behavior of the solid hydroperoxylated polypropylene fiber with NO is consistent with the conclusions listed above.

6 RECOMMENDATIONS

The results presented in this thesis indicate that organic hydroperoxides can be successfully used to quantitatively remove nitric oxide. The influence of various operating conditions on NO removal rate were determined. A nitrogen balance was carried out for the case of 0.3 M p-menthane hydroperoxide reacting with 1500 ppm NO over a 3.5 hour period on the basis that menthane nitrate is the only product. Research still needs to be conducted in the following areas:

* Product analyses, nitrogen balances, and reaction pathway for pinane, cumene, polypropylene, and possibly 3,6-dimethyl-3-octyl hydroperoxide

* Detection of H_2 , H_2O , or N_2O formation to help identify a possible mechanism

* The effect of temperatures above 100^oC with p-menthane, pinane, cumene, and polypropylene hydroperoxide

* Reactions of NO in the presence of typical amounts of other flue gases, such as O_2 , CO_2 , NO_2 and SO_2

* Kinetic studies of these reactions including NO absorption rates and overall mass transfer coefficients

* The eventual scale-up to pilot plant operations

* Study of denitration and regeneration of the hydroperoxides

7 HYDROPEROXYLATED POLYPROPYLENE FIBER STUDIES

The oxidizing ability of hydroperoxylated polypropylene fiber was also studied in our research.

7.1 Experimental

7.1.1 Materials

Two hydroperoxylated polypropylene fiber samples were provided by Dr. David Carlsson of the Institute for Environmental Chemistry, National Research Council of Canada. Both samples were prepared by taking "Herculon" "white staple" 1.8 denier (17 u diameter) polypropylene (PP) fiber obtained from Hercules, Inc. and exposing them at 0.7 Mrad/h of 60 Co ν -rays in air at about 40°C. Total irradiation time was 25 hours in each case and was selected (based on previous test runs) to give a high degree of hydroperoxide formation. From iodometric analysis of PP film, ν -oxidized under the same conditions, films and fiber have 0.38 and 0.42 mole in hydroperoxide per kg fiber, respectively.

7.1.2 Procedure

The fiber samples were packed in a 56 cm long glass column 2.54 cm in diameter. Different length of packed fiber were obtained by changing the fiber mass.

7.2 Results and Discussion

A number of experiments were carried out to test the NO removal rate with hydroperoxylated polypropylene fiber at different reaction temperatures, fiber masses and gas flow rates. Results shown in Table 11.

Table 11. NO Removal with HydroperoxylatedPolypropylene Fiber

Fiber maes, g	-OOH group, mole	Gas flow rate, cc/min	Temperature, ⁰ C	Conversion, %
4.80	1.82•10^-3	60	25	0
4.80	1.82•10^-3	60	70	9.8
4.80	1.82•10^-3	60	80	18.3
8.69	3.30•10^-3	60	70	19.5
14.58	6.12•10^-3	20	25	0
14.58	6.12•10^-3	20	50	20.6
14.58	6.12•10^-3	20	80	77.5
17.40	6.61•10^-3	60	25	0
17.40	6.61•10^-3	60	50	6.6
17.40	6.61•10^-3	60	70	23.3
17.40	6.61•10*-3	60	80	47.2

NO inlet concentration = 1100 ppm

Operating time = 6 hours

As these results indicate, the trend with temperature, fiber mass, and gas flow rate on NO removal is similar as that for liquid organic hydroperoxides. That is, higher conversion of NO can be reached at higher temperature, higher fiber mass and lower gas flow rate.

The conversion as a function of reaction time was also studied, a breakthrough curve for NO oxidation with hydroperoxylated polypropylene is shown in Figure 23.

7.3 Conclusion

High conversion of NO can be achieved at high temperatures, high concentrations of hydroperoxide group, and low gas flow rates with hydroperoxylated polypropylene fibers as oxidizers.

7.4 Recommendation

Continue research to help understand how the solid-gas reaction occurs.

Figure 23. Breakthrough Curve for Hydroperoxylated Polypropeylene Fiber at 80°C



NO concentration = 1100 ppm Gas flow rate = 20 cc/min -OOH group on the fiber = 6.12+10^-3 mole

8 REFERENCES

- Anderson, L. G., (1983), "Fate of Nitrogen Oxides in Urban Atmospheres" Trace Atmospheric Constituents Wiley, New York, Ch9.
- Atkinson, R. and A. C. Lloyd, (1984), "Evaluation of Kinetic and Mechanistic Data for Modeling of Photochemical Smog" J. phys. Chem. Kinet., 16 1175.
- Atkinson, R., S. M. Aschmann, W. P. L. Carter, A. M. Winer, and J. N. Pitts, Jr., (1982), "Alkyl Nitrate Formation from the NO_x-Air Photooxidations of C₂-C₈ n-Alkanes" J. Phys. Chem., 86, 4563.
- Atkinson, R., S. M. Aschmann, W. P. L. Carter, A. M. Winer, and J. N. Pitts, Jr., (1984), "Formation of Alkyl Nitrates from the Reaction of Branched and Cyclic Alkyl Peroxy Radicals with NO" Int. J. Chem. Kinet., 16,1085.

Balla, R. J., (1985), "Kinetics of the Reactions of Iso-propoxy Radicals with NO, NO₂, and O₂" Chem. Phys. 99, 323.

Barlettano, W., (1991), unpublished work.

Bhatia, S. C. and J. H. Hall, Jr., (1980), "A Matrix-Isolation-Infrared Spectrospic Study of the Reaction of Nitric Oxide with Oxygen and Ozone" J. Phys. Chem., Vol. 84, 3255.

Bienstock, D., (1972), "Control of NO_X Emission in Coal Firing" Industrial Coal Conference, Purdue University.

Bluhm, A. L., (1976), "Chemical Characterization of Nitrocellu-

lose Degradation Products" Technical Report 76-46-FSL, U. S. Army.

- Borders, R. A., (1982), "A Direct Determination of the Activation Energy of Nitric Oxide with Ozone" Diss. Ahstr. Int. B 1982, 42(9), 3674.
- Carlsson, D. J., R. Brousseau, Can Zhang, and D. M. Wiles, (1986), "Polyolefin Oxidation: Quantification of Alcohol and Hydroperoxide Products by Nitric Oxide Reactions" Polymer Degradation and Stability 17, 303-318.
- Carlsson, D. J., R. Brousseau, Can Zhang, and D. M. Wiles, (1988), "Indentification of Products from Polyolefin Oxidation by Derivatization Reactions" ACS Symposium Series 364, Ch. 27, pp 376.
- Carter, W. P. L. and R. Atkinson, (1985), "Atmospheric Chemistry of Alkanes" J. Atmos. Chem., in Press.

Clyne, M. A. A. and B. A. Thrush, (1961), Nature, 189, 56.

- Clyne, M. A. A. and B. A. Thrush, (1962), Discussions Faraday Soc., 33, 139.
- Darnall, K. R., W. P. L. Carter, A. M. Winer, A. C. Lloyd, and J. N. Pitts, Jr., (1976), "Importance of RO_2 + NO in Alkyl Nitrate Formation from C_4 - C_6 Alkane Photooxidations under Simulated Atmospheric Conditions" J. Phys. Chem., 80, 1948.

Dogliotti, L. M., R. C. Chalk, L. A. Spano, and D. H. Sieling, (1974), "Decomposition of Nitrocellulose using Aqueous Ammonia" Technical Report TR-75-14-FSL, U. S. Army. Finlayson-Pitts, B. J., J. N. Pitts, Jr., (1986), "Atmospheric

Chemistry" A Wiley-Interscience, New York, pp. 160-163, 419-430, 522-526, 598-600, 971-972.

- Flagan, R. C. and J. H. Seinfeld, (1988), "Fundamentals of Air Pollution Engineering" Prentice-Hall, Englewood Cliffs, New Jersey.
- Foreman, R. W. and H. P. Lankelma, (1957), J. Am. Chem. Soc., 79, 409.
- Gilmont, E. R. and H. K. LatoureHe, Br. Pat. 904, 475, 1962 [CA 58, 3318b, 1963]
- Glich, H. S., J. J. Klein, and W. Squire, (1957), J. Chem. Phys., Vol. 27, p. 850.
- Hampson, R. F., Jr. and D. Garvin, (1978), "Reaction Rate and Photochemical Data for Atmospheric Chemistry-1977" National Bureau of Standards Spec. Publ. 513.

Harcourt, R. T., (1972), J. Mol. Struct, Vol. 11.

- Harteck, P., (1933), "The Preparation of HNO or (HNO)_n" Ber., 66B, 423-6.
- Hikita, (1977) J. Chem. Eng. Japan. Vol. 11, 360.
- Hoffman, M. Z. and R. B. Bernstein, (1960), J. Phys. Chem., 64, 1753.
- Irving, P. M., (1991), "Acidic Deposition: State of Science and Technology" U. S. National Acid Precipitation Assessment Program.
- Isom, B. G., S. D. Dennis, and J. M. Bates, (1984), "Impact of Acid Rain and Deposition on Aquatic Biological Systems" ASTM STP 928.

- Jahnig, C. and H. Shaw, (1981), "A Comparative Assessment of Flue Gas Treatment Process, Part I - Status and Design Basis" Journal of the Air Pollution Control Association 31, 421-428.
- Jahnig, C. and H. Shaw, (1981), "A Comparative Assessment of Flue Gas Treatment Process, Part II - Environmental and Cost Comparison" Journal of the Air Pollution Control Association 31, 540-541.
- Kann, J., R. Kalue, and A. Kass, (1977), "Oxidation of Nitric Oxide by Potassium Permanganate" Tr. Tallin. Politekh. Inst. 1976, 402, 65-9 (Russ).
- Ladhabhoy, M. E. and M. M. Sharma, (1969), "Absorption of Oxygen by n-Butylaldehyde" J. Appl. Chem., Vol. 19, 267.

Lahiri, R. N., (1981) Indian Chemical Engineer, Vol. 23, 44.

- Levine, J. S., T. R. Augustsson, I. C. Anderson, J. M. Hoell, Jr., and D. A. Brewer, (1984), "Tropospheric Sources of NO_X: Lightning and Biology" Atmospheric Environment Vol. 18 No. 9. p. 1797.
- Littlejohn, D. and S. G. Chang, (1990), "Removal of NO_x and SO₂ from Flue Gas by Peracid Solutions" Ind. Eng. Chem. Res. 29, 1420-1424.
- Lynn, D. A., (1976), "Air Pollution: Threat and Response" Addison-Wesley pp. 104.

Makansi, J., (1988), "Reducing NO_x Emissions" Power, Sept..

Maulbetsch, J. S., (1986), "Retrofit Control Options for Coal Fired Electric Utility Power Plants" Journal of Air Pollution

Control Association Vol. 36. No. 1294.

- Noyes, W. A., J. S. Hammond, and J. N. Pitts, Jr., (1968), "Advances in Photochemistry" John Wiley & Sons, New York.
- Sada, E., H. Kumazawa, and N. Hayakawa, (1977), Chem. Eng. Sci. Vol. 32, 1171.
- Sada, E. and H. Kumazawa, (1978), Chem. Eng. Sci. Vol. 33, 315.
- Sada, E. and H. Kumazawa, (1979), "Absorption of Lean NO_x in Aqueous Solution of NaClO₂ and NaOH" Ind. Eng. Chem. Proc. Des. Develop, Vol. 18, 275.
- Shaw, H., (1974), "The Effects of Water, Pressure, and Equivalence Ratio on Nitric Oxide Production in Gas Turbines" Transactions of the ASME, July 1974, 240-246.
- Shaw, H., (1976), "Aqueous Solution Scrubbing for NO_X Control in Munitions Incineration" Winter Annual ASME Meeting, New York, Paper NO. 76-WA/Fu-9 (1976)
- Shelton, J. R. and R. F. Kapczewski, (1967), "Nitric Oxide Induced Free-Radical Reactions" J. Org. Chem., 32, 2908.
- Singh, H. B., (1987), "Reactive Nitrogen in the Troposphere; Chemistry and Transport of NO_X and Pan" Environ. Sci. Tech nol. Vol 21.

Smallwood, H. M., (1929), J. Am. Chem. Soc., 51, 1985.

- Sommerlad, R. E., (1971), "Nitrogen Oxides Emission-An Analytical Evaluation of Test Data" 33rd Annuel Meeting. The American Power Conference, Chicago.
- Swern, D., (1972), "Oganic Hydroperoxides" Wiley-Interscience, New York, Ch. 2.

- Szmant, H. H., (1989), "Organic Building Blocks of the Chemical Industry" Wiley-Interscience, New York, pp. 330-342.
- Takahashi, S., A. Shigeru, T. Tomoyuki, A. Hidetoshi, and H. Takao, (1979), "Oxidation of Nitrogen Monoxide in a Waste Gas" Jpn. Kokai Tokkyo Koho 79 39,095.

Taylor, H. A. and C. Tanford, (1944), J. Chem. Phys., 12, 47.

Topol, L. E., (1968), "A Study of the Nitric Oxide Concentrated

Sulfuric Acid Reaction" J. Inorg. Nucl. Chem. Vol. 30, 2977.
Uchida, S., T. Kobayashi, and S. Kageyama, (1983), "Absorption of Nitrogen Monoxide into Aqueous KMnO₄/NaOH and Na₂SO₃/FeSO₄ Solution" Ind. Eng. Chem. Process Develope, Vol. 22, 323.
Wenger, C., (1990), unpublished work.

- Yang, C. L., (1990), "Aqueous Absorption of NO_X Induced by Sodium Chlorite Oxidation" Master Thesis, NJIT.
- Yang, C. L., H. Shaw, and J. J. Weir, (1991) "Aqueous Absorption of NO_x Promoted by Strong Oxidizing Agents" presented at the Symposium of offgas from Municipal Waste Incineration, 1991 AICHE Summer National Meeting, Pittsburgh, PA, Paper NO. 22d, August 18-21.
- Zeldovich, J., (1946), "The Oxidation of Nitrogen in Combustion and Explosives" Acta Physicochimica U.S.S.R., Vol. 21, p. 577.