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# The synthesis and decomposition of O-substituted phenylhydroxylamines

Helen Carol Kennicott

*Union College - Schenectady, NY*

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The Synthesis and Decomposition  
of O-substituted Phenylhydroxylamines

by

*Carol*  
Helen C. Kennicott, *UC 1976*  
*14*

Submitted in partial fulfillment  
of the requirements for  
Honors in the Department of Chemistry  
UNION COLLEGE  
March, 1976



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# ABSTRACT

KENNICOTT, HELEN C. The synthesis and decomposition of O-substituted phenylhydroxylamine. Department of Chemistry, March 1976.

O-(phenyl)hydroxylamine and its p-nitrated derivative were synthesized for use in a study of substitution reactions at an  $sp^3$  hybridized nitrogen atom. The O-(phenyl)hydroxylamine was decomposed thermally in several nonnucleophilic solvents and in water, with base present. It is proposed that in organic solvents, the decomposition proceeds by a radical mechanism involving a solvent cage intermediate. Ammonia and aminophenols are the major products. In water, it appears that an  $S_N1$  reaction producing phenoxide may compete with the radical mechanism.



This thesis is dedicated, with love, to my parents,  
Dr. and Mrs. Philip R. Kennicott.



## ACKNOWLEDGMENT

I would like to thank Dr. Leslie A. Hull for his advice and help during this research and my mother for her help with the typing of this thesis.



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## INTRODUCTION

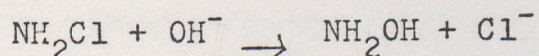






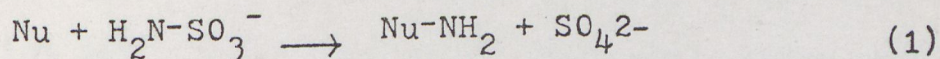
and chloramines. The nucleophilic reactivity of the attacking species and thus the rate of reaction can be increased by substituting methyl groups for the hydrogen atoms on ammonia. Yagil and Anbar conclude that the  $S_N2$  reactions of alkyl halides and ammonia are analogous to the reaction of chloramine and ammonia.

Anbar and Yagil<sup>2</sup> also investigated the hydrolysis of chloramines. Hydroxylamine was found as the primary product, and the kinetics of the reaction were determined to be second order. Nucleophilic substitution of  $Cl^-$  by  $OH^-$  is suggested:



Noble<sup>3</sup> used measurements of activation volumes for the above reaction to confirm the bimolecular displacement mechanism.

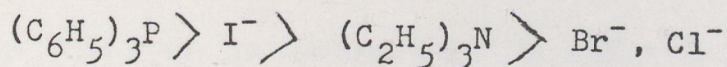
More recently, work on the kinetics of nitrogen substitution reactions has been performed using hydroxylamine-O-sulfonic acid. Several different nucleophiles have been used to study the kinetics of the following reaction:



In one study, Krueger et al.<sup>4</sup> used  $I^-$ ,  $(C_6H_5)_3P$  and  $(C_2H_5)_3N$  as nucleophiles and they found nucleophilic attack on the nitrogen atom to be the principal step in all cases. They gave the following order of nucleophilicities



towards the trivalent nitrogen:



Polarizability and ease of oxidation of the nucleophile seem most important, with basicity playing a minor role, in determining the order of nucleophilicity.

Krueger et al.<sup>4</sup> also found that the rate of reaction is sensitive to substitution of the hydrogen atoms on  $\text{H}_3\text{N}^+\text{OSO}_3^-$  by methyl groups. When methyl groups are added the reactivity of  $\text{H}_3\text{N}^+\text{OSO}_3^-$  towards iodine decreases, due to either steric effects or electron donation by the methyl groups. Since electron withdrawing groups such as  $\text{C}_6\text{H}_5^-$  or  $\text{SO}_3^-$  also decrease the reactivity, the steric effect is presumed to dominate.

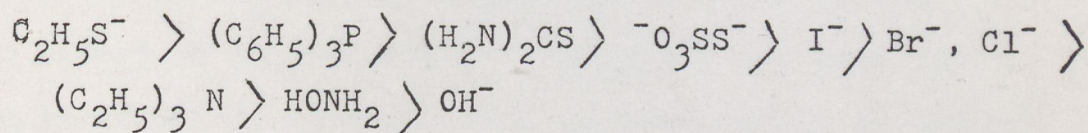
In a later work, Krueger, Sudbury and Blanchet<sup>5</sup> investigated the same reaction using ethanethiolate, hydroxylamine and hydroxide as nucleophiles. They found that the order of nucleophiles is also the order of soft bases, and they suggest that nitrogen is a soft electrophilic center. The effect of the leaving group on the rate of reaction was also investigated; increased proton basicity of the leaving group decreases the reactivity of the nitrogen compound.

The solvent effect on the leaving group was investigated by Krueger et al.<sup>6</sup> for reaction (1). In a dimethyl sulfoxide water system, the rate of reaction decreased

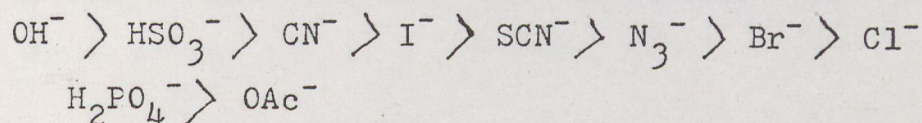


as the ratio of dimethyl sulfoxide to water was increased. It was suggested therefore, that  $\text{SO}_4^{2-}$  is the leaving group and its increased stabilization in water accounts for the higher rate of reaction.

Additional results from another study by Krueger et al.<sup>7</sup> using thiourea and thiosulfate as nucleophiles gave the following overall order of nucleophilicities:



Yap et al.<sup>8</sup> also determined an order of relative nucleophilicities when they investigated the reaction of various anions with difluoramine:



Both of these lists of nucleophilicities agree qualitatively with the order of nucleophilicity towards  $\text{sp}^3$  hybridized carbon. The exception is  $\text{OH}^-$  in the study by Yap et al.<sup>8</sup>, and they suggest that it could be reacting by a different mechanism.

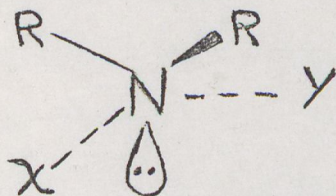
Although the substitution reactions of various nucleophiles at an  $\text{sp}^3$  hybridized nitrogen atom seem very similar to  $\text{S}_{\text{N}}2$  reactions at carbon, some unique properties of the electrophilic nitrogen center should be considered.

Anbar and Yagil<sup>1</sup> found that the different methyl substituted chloramines,  $\text{H}_2\text{N}-\text{Cl}$ ,  $(\text{CH}_3)\text{HN}-\text{Cl}$ ,  $(\text{CH}_3)_2\text{N}-\text{Cl}$



all react at about the same rate, and this finding was later confirmed by Noble<sup>3</sup>. In an investigation by Oae and Yamamoto<sup>9</sup>, O-(2,4-dinitrophenyl)hydroxylamine was used as a substrate, and was treated with various nucleophiles to investigate  $S_N2$  reactions at nitrogen. Here again, it was found that the nitrogen atom was not nearly as sensitive as the  $sp^3$  hybridized carbon atom to the steric effect of nucleophiles. Presumably the lone pair of electrons on the nitrogen atom is more easily distorted than a  $\sigma$  bond to a carbon atom.

Paquette and Farley<sup>10</sup> also discuss the absence of a steric effect in nitrogen substituted compounds and suggest that a non-collinear attack that minimizes repulsion with the R groups may be occurring:



They find that the reaction is subject to some steric control when very bulky nucleophiles are used.

In their paper, Paquette and Farley also discuss electrostatic differences between  $S_N2$  reactions involving nitrogen and carbon. It is assumed that the nitrogen atom will tolerate less positive charge than a carbon atom in a transition state because of its increased electronegativity. Presumably the extent of bond making and breaking could differ in the transition states for nitrogen and carbon  $S_N2$  reactions, due to the different electro-

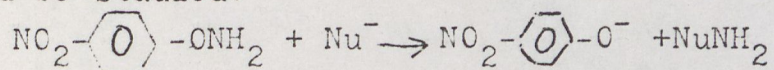


static conditions at the central atom.

Another property of some nitrogen compounds that is not present in similar carbon components is the enhanced reactivity of molecules where two atoms with lone pairs of electrons are adjacent to each other. This property is termed the  $\alpha$ -effect and is attributed by Aubort and Hudson<sup>11</sup> to repulsion between two  $p_\pi$  orbitals. The two  $p_\pi$  orbitals overlap with resultant orbital splitting and an increase in energy for the highest orbital. It is suggested that this splitting of the orbital can affect properties such as redox potential and polarizability of the molecule.

Bond breakage in a molecule which has substantial  $p_\pi$ - $p_\pi$  overlap is favored because of the decrease in electron repulsion that will occur.

The purpose of this study was to continue the investigation of substitution reactions at nitrogen and their kinetics. To this effect, the synthesis of O-(p-nitrophenyl)hydroxylamine was attempted. It was desired to obtain this compound so that the following reaction could be studied:



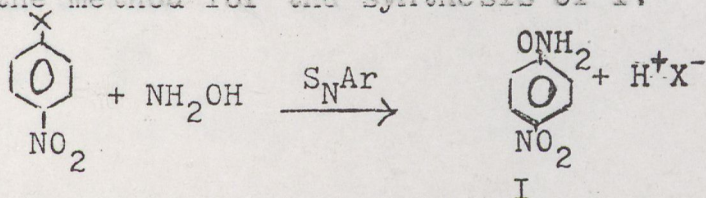
Concentration of p-nitrophenoxide throughout the course of the reaction could be monitored by ultraviolet absorption spectroscopy. The p-nitrophenolate anion should be a



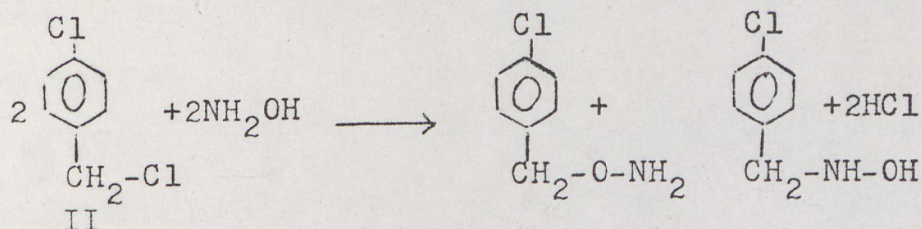
good leaving group since it is a relatively weak base and because the O-N bond in O-(p-nitrophenyl)hydroxylamine is weak due to repulsion between unshared pairs of electrons.

Previous attempts at synthesizing O-(2,4-dinitrophenyl)hydroxylamine by R. Sommers<sup>12</sup> were not successful. It was thought that the compound was difficult to isolate under the acidic conditions in which it was formed, due to its instability caused by two strongly electrophilic nitrogen groups on the ring. The mono-substituted compound should be more stable and thus easier to obtain.

Reaction of a 4-nitro, 1-halobenzene with hydroxylamine to give the product by an  $S_NAr$  mechanism was chosen as the method for the synthesis of I.



Previous model studies by Sommers to determine the best conditions for reaction of  $\alpha$ ,p-dichlorotoluene with hydroxylamine were available:

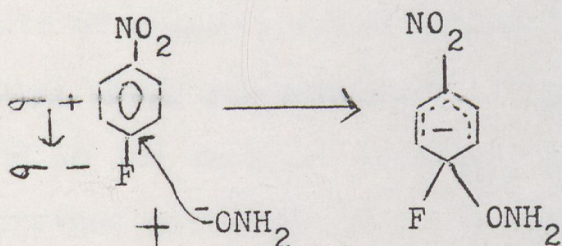


O-substitution of hydroxylamine is maximized when the reaction is run under basic conditions. Presumably



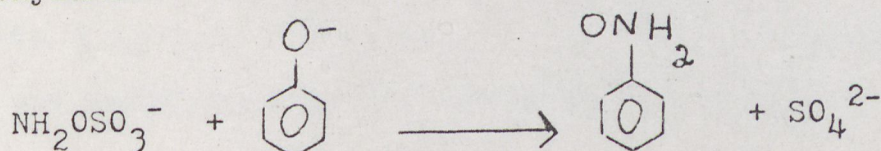
$\text{NH}_2\text{O}^-$ , a stronger nucleophile than  $\text{NH}_2\text{OH}$ , is the attacking species in the presence of a strong base. It was realized that under these conditions, nucleophilic attack on II by the strong base might compete with attack by  $\text{NH}_2\text{O}^-$ .

Both 4-nitro-1-chlorobenzene and 4-nitro-1-fluorobenzene were reacted with neutral and basic solutions of hydroxylamine under various conditions. The fluoro compound was expected to be the more reactive compound. The more electronegative -F group should create a stronger partial positive charge at the site of attack by the negatively charged nucleophile:



Only the reaction involving the fluoro compound and the basic hydroxylamine solution yielded a product. The product, a yellow solid melting at  $183\text{--}185^\circ\text{C}$ , could not be identified.

An alternative synthesis of I, according to the method of Bumgardner and Lilly<sup>13</sup>, was attempted. The parent compound, O-(phenyl)hydroxylamine was prepared by them, using hydroxylamine-O-sulfonic acid and phenoxide:





The compounds O-(p-methylphenyl)hydroxylamine hydrochloride and O-(m-chlorophenyl)hydroxylamine hydrochloride were prepared in a similar manner by Bauer and Dalalian<sup>14</sup>. The conditions of the reaction were extended to give a successful synthesis of the hydrochloride salt of I. The yield, however, was quite poor, so O-(phenyl)hydroxylamine hydrochloride was prepared for use in kinetic and decomposition studies.

The nature of the decomposition of O-(phenyl)hydroxylamine in several solvents was studied. The amount of basic gas produced by the decomposition at the boiling points of cumene, chlorobenzene, hexane, decane, and ethanol/water was measured. Dilute solutions of the compound in the various solvents were refluxed under nitrogen, to prevent air oxidation. Any gases given off were swept into a standard acid solution which was then titrated.

The decomposition was also performed at two different concentration levels in cumene, to determine if the mechanism depended on the initial concentration of O-(phenyl)hydroxylamine.

The kinetics of the decomposition of O-(phenyl)hydroxylamine in water or water/ethanol were measured using UV absorption spectroscopy. The absorption of the solution was measured from 250-350 nm; a plot of

$\log [a_0 - a_\infty] / [a_t - a_\infty]$  vs. time was made, where  $a$  is the absorption at the wavelength of maximum absorp-



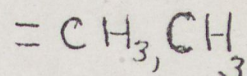
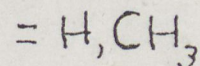
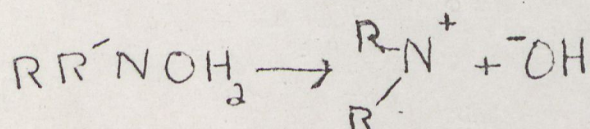
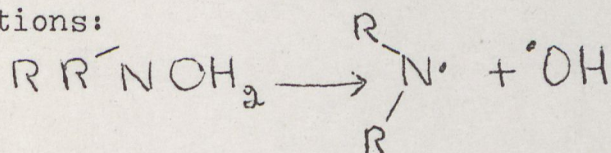
tion for the phenoxide ion. A first order rate constant for each reaction was calculated from the slope of the plots.

The decompositions were again performed under nitrogen and at the boiling point of the solvents. Reaction conditions, including the concentration of starting materials and the presence of different bases, were varied to give information about the mechanism of decomposition in a nucleophilic solvent.

The reaction was run using three different concentrations of O-(phenyl)hydroxylamine with equimolar potassium carbonate present in the solution. The concentration of O-(phenyl)hydroxylamine was then fixed, and the concentration of either  $\text{CO}_3^{2-}$  or  $\text{OH}^-$  in the solution was allowed to vary.

An attempt at identifying the products of the decomposition was made by taking IR and NMR spectra of the products of the decomposition of O-(phenyl)hydroxylamine in chlorobenzene and in decane. These two solvents were chosen so that the entire NMR scale could be monitored without interference from the solvent.

A final aspect of this project involved some theoretical predictions of the  $\Delta H$ 's for the following reactions:





A semiempirical SCF-MO method, known as MINDO/3<sup>15</sup> was used to calculate the heats of formation for the reactants and products in the above reactions. The heats of reaction were then calculated using the relation:

$$\Delta H = \sum H_{f \text{ products}} - \sum H_{f \text{ reactants}}.$$

MINDO/3 is a computer program that calculates molecular geometries and heats of formation for molecules by minimizing their energy with respect to all geometrical parameters. The calculation is based on an extension of the Pople SCF-MO method to include all the valence electrons. The modified neglect of differential overlap involves neglect of certain electron repulsion integrals involving differential overlap. The remaining integrals are then set equal to parametric functions with numerical parameters that can be varied to fit existing data.



EXPERIMENTAL



1. Synthesis of p-nitroanisole: A sodium methoxide solution was made by adding 11 g of sodium to 500 ml of methanol. The molarity of the solution was found by titrating with standard acid to be .954 M. Two g (.013 mol) of p-nitrochlorobenzene were added to 20 ml of .954 M sodium methoxide (.019 mol), in a 100 ml round bottom flask equipped with a reflux condenser. After refluxing for 12 hrs the reaction was 60% complete, as determined from the peak integration of the NMR spectra of the product, p-nitroanisole. Refluxing for another 12 hrs brought the reaction to completion.

2. Attempted synthesis of O-(p-nitrophenyl)hydroxylamine from p-nitrochlorobenzene: A neutral solution of hydroxylamine in methanol was prepared by reacting 220 ml of .954 M  $\text{NH}_2\text{OH}\cdot\text{HCl}$  with 220 ml of .954 M sodium methoxide to give a solution of .477 M  $\text{NH}_2\text{OH}$ . Also prepared, was a solution of hydroxylamine with 10% excess base by adding 190 ml of .954 M  $\text{NH}_2\text{OH}\cdot\text{HCl}$  to 210 ml of .954 M sodium methoxide to give hydroxylamine concentration of .435 M. The following reaction conditions for the synthesis of O-(p-nitrophenyl)hydroxylamine from p-nitrochlorobenzene and hydroxylamine were used:

a. Two g (.013 mol) of p-nitrochlorobenzene in 40 ml of methanol were added to 55 ml of .477 M neutral hydroxylamine solution in a round bottom flask. The resultant con-



concentrations of the two reactant species were .14 M p-nitrochlorobenzene and .28 M hydroxylamine. The reaction mixture was allowed to stand overnight, with stirring.

b. Two g. (.013 mol) of p-nitrochlorobenzene in 40 ml of methanol were added to 60 ml of .453 M hydroxylamine with excess base solution. The concentrations of reactants after mixing were .13 M p-nitrochlorobenzene and .27 M " $\text{NH}_2\text{O}^-$ ". The reaction mixture was allowed to stand overnight, with stirring.

c. An identical solution to the one described in b. (above) was prepared and allowed to reflux overnight.

The work-up procedure for the reactions is described below:

The reaction mixture was diluted with twice the volume of water and was then extracted twice with 100 ml portions of chloroform. The chloroform extracts were treated with dilute acid and were dried over  $\text{CaCl}_2$ . The acid extracts were washed with a small portion of chloroform, which was added to the original chloroform extract. The acid solution was then neutralized with dilute base and extracted with two 100 ml portions of chloroform. This chloroform extract was dried over  $\text{CaCl}_2$ , and solvent was removed from both extractions under vacuum to give the basic and neutral species present in the reaction mixture. For all three reactions, no product could be isolated and most of the starting material was recovered from the chloroform extract containing neutral species. Identification of the starting



material was made from NMR spectra.

3. Attempted synthesis of O-(p-nitrophenyl)hydroxylamine from p-nitrofluorobenzene: In addition to reacting the fluoro compound with basic and neutral solutions of hydroxylamine at room temperature and at reflux, the reaction was attempted with more concentrated solutions of hydroxylamine in the presence of 10% excess base. The following reaction conditions were utilized:

a. Two g (.014 mol) of p-nitrofluorobenzene in 40 ml of methanol were added to 58 ml of .477 M (.028 mol) neutral hydroxylamine to give concentrations of .14 M and .28 M for the reactants, respectively. The solution was allowed to stand overnight, with stirring.

b. Two g (.014 mol) of p-nitrofluorobenzene in 40 ml of methanol were added to 60 ml of .453 M hydroxylamine (.027 mol) in excess base to give concentrations of .14 M and .27 M for the reactants, respectively. The solution was allowed to stand overnight, with stirring.

c. An identical solution to the one described in b. (above) was prepared and allowed to reflux overnight.

d. Two g (.014 mol) of p-nitrofluorobenzene in 20 ml of methanol were added to 30 ml of .91 M basic hydroxylamine solution (.027 mol) to give concentrations of .28 M and .54 M for the reactants, respectively. The solution was allowed to reflux overnight.



e. Two g (.014 mol) of p-nitrofluorobenzene in 20 ml of methanol were added to 15 ml of 1.8M basic hydroxylamine (.027 mol) to give concentrations of .4 M and .8 M for the reactants, respectively. The solution was allowed to reflux overnight.

f. Two g (.014 mol) of p-nitrofluorobenzene in 20 ml of methanol were added to 15 ml of 2.27 M basic hydroxylamine solution to give concentrations of .4 M and 1.0 M for the reactants respectively. The solution was allowed to reflux overnight.

g. Four g (.028 mol) of p-nitrofluorobenzene were added directly to 60 ml of .91 M basic hydroxylamine (.055 mol) to give concentrations of .5 M and .9 M for the reactants, respectively. The solution was allowed to reflux overnight.

The work-up procedure for the above reactions was the same as that already described for the reactions involving the chloro compound. No noticeable product was formed from the reactions using the neutral solutions of hydroxylamine. However, the reactions involving the 10% excess base hydroxylamine solutions gave small amounts of an orange solid, m.p. 180-185°C. Recrystallization from benzene gave a yellow solid, m.p. 183-185, which has not been identified.



Table 1

Summary of Reaction Conditions of p-Nitrohalo Compounds and Hydroxylamine

	<u>Reactant</u>	<u>Concentration</u>	<u>Condition</u>	<u>Product</u>
1.	p-nitrochlorobenzene neutral $\text{NH}_2\text{OH}$	.14 M .28 M	stand overnight	none
2.	p-nitrochlorobenzene $\text{NH}_2\text{O}^-$ ; excess base	.43 M .27 M	stand overnight	none
3.	p-nitrochlorobenzene $\text{NH}_2\text{O}^-$ ; excess base	.13 M .27 M	reflux overnight	none
4.	p-nitrofluorobenzene neutral $\text{NH}_2\text{OH}$	.14 M .28 M	stand overnight	none
5.	p-nitrofluorobenzene $\text{NH}_2\text{O}^-$ ; excess base	.14 M .27 M	stand overnight	none
6.	p-nitrofluorobenzene $\text{NH}_2\text{O}^-$ ; excess base	.14 M .27 M	reflux overnight	yellow solid
7.	p-nitrofluorobenzene $\text{NH}_2\text{O}^-$ ; excess base	.28 M .54 M	reflux overnight	yellow solid
8.	p-nitrofluorobenzene $\text{NH}_2\text{O}^-$ ; excess base	.4 M .8 M	reflux overnight reflux overnight	yellow solid yellow solid
9.	p-nitrofluorobenzene $\text{NH}_2\text{O}^-$ ; excess base	.4 M 1.0 M	reflux overnight	yellow solid
10.	p-nitrofluorobenzene $\text{NH}_2\text{O}^-$ ; excess base	.5 M .9 M	reflux overnight	yellow solid



4. Synthesis of O-(phenyl)hydroxylamine from hydroxyl-O-sulfonic acid and potassium phenoxide: <sup>13</sup>

1. Synthesis of hydroxylamine-O-sulfonic acid: <sup>16</sup> 62 ml of 30% fuming sulfuric acid were placed in a dry 500 ml three neck round bottom flask. The flask was equipped with paddle stirrer and a thermometer, vented through a drying tube. 32 g (.16 mol) of dry, well-ground bis(hydroxylammonium)sulfate were added slowly to the sulfuric acid with continuous stirring. The reaction mixture was allowed to stand for one hr, with stirring, at room temperature. It was then cooled to 0°C and cold, anhydrous ether was added very slowly. After addition of the ether the mixture was cooled to 15°C and was filtered through a sintered glass funnel. The white solid was collected, dried overnight under vacuum and stored in a desiccator over concentrated sulfuric acid. The yield of hydroxylamine-O-sulfonic acid was 42.1 g (.37 mol), 96%, and it was assumed to have a purity of 95% for future work.

2. Synthesis of O-(phenyl)hydroxylamine hydrochloride: A solution of potassium phenoxide was made by dissolving 56.4 g (.6 mol) of phenol and 33.6 g (.6 mol) of potassium hydroxide in 420 ml of water. The potassium phenoxide solution and 200 ml of methylcyclohexane were placed in a one liter round bottom flask, equipped with a reflux condensor and a paddle stirrer. A solution of 17 g (.15 mol) of hydroxylamine-O-sulfonic acid in 40 ml of water was added slowly over ten minutes as the reaction mixture was heated under reflux.



The mixture was then cooled in an ice bath and the layers were separated. The water layer was extracted twice with ether and the combined ether and methylcyclohexane solution was washed with aqueous sodium hydroxide. The solution was then washed twice with water and was dried over magnesium sulfate. The ether was removed under vacuum, and hydrogen chloride, generated by adding sodium chloride to concentrated sulfuric acid, was bubbled through the solution. A pinkish solid precipitated upon acidification, which was collected by filtration. Between two and four g (.014-.028 mol) of the product were recovered, giving a yield of 9-18%. The product, after having dried for half an hour under vacuum, decomposed at 95-105°C. Recrystallization from ethyl acetate gave light pink crystals, decomposing at 126°C, ref. 136°C<sup>14</sup>. During the recrystallization process, hydrogen chloride was passed through the mother liquor to aid in the precipitation of the O-(phenyl)hydroxylamine hydrochloride. Identification of the product was confirmed by its IR spectra in a Nujol mull.

5. Synthesis of O-(p-nitrophenyl)hydroxylamine hydrochloride:

A solution of potassium p-nitrophenoxide was made by dissolving 42 g (.3 mol) p-nitrophenol in 420 ml of water containing 16.5 g (.3 mol) potassium hydroxide. A solution of 8.5 g (.075 mol) of hydroxylamine-O-sulfonic acid in 20 ml water was reacted with the potassium p-nitrophenoxide, as described under the synthesis of O-(phenyl)hydroxylamine hydrochloride.



After acidification of the methylcyclohexane solution, 0.3 g (.0015 mol), 2% yield, of a white solid were collected. The solid, melting at  $136^{\circ}\text{C}$ , was identified as O-(p-nitrophenyl)-hydroxylamine hydrochloride by its IR spectra.

#### Thermal Decomposition of O-(phenyl)hydroxylamine

1. Thermal decomposition in cumene: O-(phenyl)hydroxylamine was decomposed thermally in purified cumene. One g (.007 mol) O-(phenyl)hydroxylamine hydrochloride was dissolved in water and treated with excess aqueous sodium hydroxide. The solution was then extracted twice with 10 ml portions of cumene. The combined cumene extracts were washed twice with water and dried over  $4\text{\AA}$  molecular sieves. The cumene had been previously purified by washing it several times with concentrated sulfuric acid until the washings remained clear. The cumene was then washed with aqueous sodium bicarbonate and twice with water. Finally, it was dried over magnesium sulfate and distilled from lithium aluminum hydride.

The solution of O-(phenyl)hydroxylamine in cumene (.35 M) was placed in a three neck 50 ml round bottom flask. The flask was equipped with a reflux condensor and a stream of nitrogen was bubbled through the solution. Purification of the nitrogen was first achieved by passing it through a saturated solution of pyrogalllic acid in water, then concen-



trated sulfuric acid and finally through a drying tube. Basic gases given off during the decomposition were trapped by passing the nitrogen stream through a flask containing 300 ml of a standardized solution of hydrochloric acid.

Decomposition of O-(phenyl)hydroxylamine was effected by heating the solution in the absence of air for 20 hrs, at the boiling point of cumene ( $152^{\circ}\text{C}$ ). Upon heating, the solution slowly turned red and then black. Work-up of the cumene solution after decomposition was first attempted by extracting the solution with several portions of aqueous sodium hydroxide. Distillation of the cumene from the remaining solution, under vacuum, was not possible due to excessive bumping of the solution. Therefore, ethanol was added to the cumene solution and a precipitate formed. A brown solid, which did not melt below  $300^{\circ}\text{C}$  was collected.

The decomposition in cumene was repeated, using a 0.035 M solution of O-(phenyl)hydroxylamine, made by treating 0.1 g (.0007 mol) of O-(phenyl)hydroxylamine hydrochloride with base and extracting with 20 ml of cumene.

2. Thermal decomposition in hexane: 0.0534 g (.0004 mol) of O-(phenyl)hydroxylamine hydrochloride were treated with aqueous base. The neutralized compound was extracted into 20 ml of hexane, that had previously been purified by distillation from lithium aluminum hydride, through a Hempel tube. The 0.02 M solution was refluxed for 20 hrs at the boiling point of hexane ( $67^{\circ}\text{C}$ ), but the solution did not change color



indicating that decomposition did not occur.

3. Thermal decomposition in decane: 0.0868 g of O-(phenyl)-hydroxylamine hydrochloride were converted to the neutralized compound as described and were dissolved in 20 ml of decane to give a 0.03 M solution. The decane had been previously purified by distillation from lithium aluminum hydride, through a Hempel tube. The solution was refluxed overnight (at 172°C), under a nitrogen atmosphere and any basic gases that were produced were trapped in a standard acid solution. Again, heating caused a slow darkening of the solution.

4. Thermal decomposition in chlorobenzene: 0.1255 g (.0009 mol) of O-(phenyl)hydroxylamine hydrochloride were treated with base and then dissolved in 25 ml of chlorobenzene to give a 0.035 M solution. The chlorobenzene had been previously purified by distillation. The solution was refluxed under nitrogen for 20 hrs (at 132°C) and basic gases were again trapped by passing the nitrogen stream through a solution of standard acid. As before, the solution darkened as decomposition proceeded.

5. Thermal decomposition in chlorobenzene, with potassium carbonate present: 0.1298 g (.0009 mol) of O-(phenyl) hydroxylamine hydrochloride were treated with base and extracted into 25 ml of purified chlorobenzene to give a 0.036 M solution. Two g of potassium carbonate were added to the solution and it was allowed to reflux (at 132°C) overnight in



a nitrogen atmosphere. Basic gases were collected in a standard acid trap and heating again caused darkening of the solution.

6. Thermal decomposition in water/ethanol: .1724 g (.0012 mol) of O-(phenyl)hydroxylamine hydrochloride were dissolved in 10 ml of water and were treated with five ml of 3 N base. The basic solution was extracted twice with ether and the ether extracts were washed twice with water and dried over magnesium sulfate. The ether was removed under vacuum and the resulting O-(phenyl)hydroxylamine was dissolved in 30 ml of 1:2 (by volume) water/ethanol to give a 0.04 M solution. An equimolar amount (.0012 mol) of potassium bicarbonate was dissolved in the solution and it was allowed to reflux overnight (at 80°C), under nitrogen. Basic gases were passed through standard acid and darkening of the solution again occurred, though not as extensively as when the decomposition was performed in non-nucleophilic solvents..

### Kinetics

The kinetics of the decomposition of O-(phenyl)hydroxylamine in a nucleophilic solvent were investigated by following the UV spectrum of the solution throughout the course of the reaction.

1. Decomposition in water/ethanol: A 0.04 M solution of O-(phenyl)hydroxylamine, with equimolar potassium carbonate, in 1:2 water/ethanol was prepared as described above. The



solution was refluxed overnight at 80°C, in a nitrogen atmosphere. 0.1-1 ml samples were periodically withdrawn from the solution and diluted with 1:2 water/ethanol. The UV spectrum of the solution, using a water/ethanol blank containing potassium bicarbonate, was recorded on a Perkin-Elmer 202 Spectrophotometer, several times throughout the course of the reaction. The absorbance at 289 nm was tabulated and corrected for dilution factors and a plot of  $\log(a_0 - a_\infty)/(a_t - a_\infty)$  vs time was made.

2. Decomposition in water— varied concentration of O-(phenyl)hydroxylamine: Solutions of O-(phenyl)hydroxylamine and equimolar potassium bicarbonate in water were prepared at three different concentrations.

A solution of .0008 M O-(phenyl)hydroxylamine was prepared by dissolving 0.1164 g (.0008 mol) of O-(phenyl)hydroxylamine hydrochloride in 100 ml of water and adding 0.221 g (.0016 mol) of potassium carbonate. This solution was heated at reflux (98°C) under a nitrogen atmosphere, overnight. Samples were periodically withdrawn and the UV spectrum of the solution, from 250-400 nm, was taken using a water blank containing .0008 M potassium carbonate. A Cary 118 Spectrophotometer was used with a zero suppression control that allowed the scale to be expanded up to 4 absorbance units, so dilutions of the samples were not necessary. After recording the absorbance of each sample it was returned to the reaction



mixture. The absorbance at three wavelengths of maximum absorption (268, 289 and 318) was tabulated and plots of  $\log(a_0 - a_\infty)/(a_t - a_\infty)$  vs time at 289 and 318 nm were made.

Solutions of .0015 M and .00038 M O-(phenyl)hydroxylamine with equimolar potassium carbonate were prepared by dissolving 0.2176 g (.0015 mol) of O-(phenyl)hydroxylamine hydrochloride in 100 ml of water (.015 M) and adding 0.412 g of potassium carbonate. Ten ml of the .015 M solution were diluted to 100 ml giving .0015 M hydroxylamine and 25 ml of this solution were diluted to 100 ml to give .00038 M O-(phenyl)hydroxylamine. These solutions were heated overnight, at reflux, in a nitrogen atmosphere. The absorbance of the solutions was read periodically, using blanks of .0015 M and .00038 M potassium carbonate. Again, absorbances at 268, 289 and 318 nm were tabulated and plots of  $\log(a_0 - a_\infty)/(a_t - a_\infty)$  were made.

3. Decomposition in water—varied concentrations of potassium carbonate: A .008 M solution of O-(phenyl)hydroxylamine hydrochloride in water and a .0032 M solution of potassium carbonate in water were prepared. A solution of .0008 M O-(phenyl)hydroxylamine and .00032 M carbonate was prepared by adding ten ml of .008 M O-(phenyl)hydroxylamine hydrochloride (.00008 mol) to 35 ml of .0032 M potassium carbonate (.00011 mol) and diluting to 100 ml. Also prepared was a .0008 M solution of O-(phenyl)hydroxylamine with .00064 M potassium carbonate, by adding 10 ml of .008 M



O-(phenyl)hydroxylamine hydrochloride (.00008 mol) to 45 ml of .0032 M potassium carbonate (.00014 mol) and diluting to 100 ml with water. These solutions were allowed to decompose and the absorbance from 250-350 nm was measured using blanks of .0003 M and .0006 M potassium carbonate, as described before.

4. Decomposition in water—varied concentrations of hydroxide: A .008 M solution of potassium hydroxide in water that had been freed of carbon dioxide by boiling, was prepared. Ten ml of .008 M O-(phenyl)hydroxylamine (.00008 mol) and 15 ml of .008 M potassium hydroxide (.00012 mol) were mixed together and diluted to 100 ml to give a solution of .0008 M O-(phenyl)hydroxylamine and .0004 M hydroxide. Similarly prepared were solutions of .0008 M O-(phenyl)hydroxylamine with .0008 M and .0016 M hydroxide by adding 20 and 30 ml of .008 M hydroxide, respectively, to 10 ml of .008 M O-(phenyl)hydroxylamine. Finally, a .0008 M solution of O-(phenyl)hydroxylamine with .008 M base was prepared by adding 10 ml of .008 M O-(phenyl)hydroxylamine hydrochloride (.0008 mol) to 11 ml of .08 M hydroxide (.0088 mol), that had been freed of carbon dioxide. These solutions were decomposed and the absorbance from 250-350 nm was measured, using hydroxide solutions as blanks, as described before.



5. Decomposition of O-(p-nitrophenyl)hydroxylamine in water: The kinetics of the decomposition of O-(p-nitrophenyl)-hydroxylamine were followed in a similar manner to that described above. A solution of .00037 M O-(p-nitrophenyl)hydroxylamine was prepared by dissolving 0.0714 g (.00037 mol) O-(p-nitrophenyl)hydroxylamine hydrochloride in 100 ml of water and diluting this solution by 1:10. 0.01034 g (.00074 mol) of potassium carbonate were added to the solution, converting the salt to the neutral compound and giving a final concentration of .00037 M carbonate.

This solution was decomposed overnight, under nitrogen. The UV spectrum from 250-400 nm was monitored, using a .00037 M potassium carbonate solution as a blank. The absorbance at 400 nm was recorded and a plot of  $\log(a_0 - a_\infty)/(a_t - a_\infty)$  was prepared.

Spectral analysis of the decomposition products of O-(phenyl)-hydroxylamine

In an attempt to identify the products of the thermal decomposition of O-(phenyl)hydroxylamine, NMR and IR spectra of the reaction products were taken. A 10% solution of O-(phenyl)hydroxylamine in both decane and chlorobenzene was prepared by dissolving 0.5 g of O-(phenyl)hydroxylamine hydrochloride in water, treating it with base and extracting with ether. The ether was removed under vacuum and the re-



maining O-(phenyl)hydroxylamine was dissolved in four to five ml of the appropriate solvent. The solutions were placed in NMR tubes and were frozen in liquid nitrogen. The tubes were then evacuated and sealed and decomposition in the absence of air was allowed to proceed by placing the tubes in refluxing solutions of decane or chlorobenzene. NMR spectra of the solutions were taken at two of three time intervals during the decomposition. Final NMR spectra of both solutions and an IR spectra of the decane solution were taken after the tubes had been heated overnight.



## RESULTS



Product analysis of the attempted synthesis of O-(p-nitrophenyl)hydroxylamine from p-nitrofluorobenzene and hydroxylamine

During the work-up procedure in the attempted synthesis of O-(p-nitrophenyl)hydroxylamine from p-nitrofluorobenzene and hydroxylamine, the yellow methanol reaction mixture turned bright red upon the initial addition of water. A red color also appeared upon neutralization of the yellow acid extracts. UV spectra of the initial water/methanol solution (after work-up), of the neutralized acid extract (after extraction with chloroform) and of the final product in chloroform were taken. The wavelengths of maximum absorption are given in Table 2.

Thin layer chromatography was used to determine the purity of the product. The support was a fluorescent silica gel sheet. Chromatography was performed on pure p-nitrofluorobenzene, on recovered starting material and on the product. Retention factors for the three substances, in different solvents are given in Table 3. In all cases only one spot was observed for the product, indicating that its purity was fairly high. The recovered starting material also showed only one spot and had the same retention factor as the pure starting material.

Analysis of basic gases formed during decomposition

For each thermal decomposition of O-(phenyl)hydroxyl-



Wave Length of Maximum Absorption of Solutions Formed During Attempted Synthesis  
of O-(p-nitrophenyl)hydroxylamine

<u>Solution</u>	<u>Wavelength of Maximum Absorption</u>	
	<u>neutral</u>	<u>with added base</u>
1. Initial water/methanol solution	360 nm	385 nm
2. Acid extract, after neutralization	263, 360 nm	no change
3. Product in chloroform	348 nm	—



Table 3

Retention Factors for Products of Attempted O-(p-nitrophenyl)hydroxylamine Synthesis

<u>Solvent System</u>	<u>Compound</u>	<u>Retention Factor</u>
1. carbon tetrachloride and ether 5:1 by volume	pure starting material recovered starting material product	.64 .64 .39
2. carbon tetrachloride and ether 1:1 by volume	pure starting material recovered starting material product	.92 .92 .87
3. chloroform	product	.78
4. ether	product	.81



amine the nitrogen stream was bubbled through a flask containing 300 ml of 0.01 M HCL solution. After decomposition, 75 ml of the solution were withdrawn and titrated with 0.1 M base. The difference in molarity of the acid solution, before and after titration, was used to calculate the percent of starting material that decomposed to give basic gases upon heating. A summary of the results is given in Table 4. The percent of basic gas given off during decomposition in cumene, decane and chlorobenzene was the same, within experimental error. Decomposition in cumene at two different concentrations also gave the same results. It is assumed that decomposition in hexane did not occur due to the low boiling point of the solvent and the lack of visible reaction in the solution upon heating. Decomposition with base present, both in chlorobenzene and water/ethanol, gave lower values for the percent of basic gas formed.

Kinetics of the decomposition of O-(phenyl)hydroxylamine and C-(p-nitrophenyl)hydroxylamine:

O-(phenyl)hydroxylamine and phenoxide have different wavelengths of maximum absorption, so UV absorption spectroscopy was a valuable means of monitoring the disappearance of reactant and the appearance of product throughout the course of the reaction. O-(phenyl)hydroxylamine absorbs at 268 nm with an absorptivity coefficient of  $\log \epsilon = 3.6$ , and phenoxide



Table 4

Reaction Conditions and Percent Basic Gas Formed During Thermal Decomposition  
in Organic Solvents

<u>Solvent</u>	<u>Concentration</u>	<u>Temperature of Reaction</u>	<u>% Basic Gas</u>
1. cumene	.35 M	152°C	21 ± 1 %
2. cumene	.035 M	152°C	21 ± 1 %
3. hexane	.02 M	67°C	0
4. decane	.03 M	172°C	20 ± 1 %
5. chlorobenzene	.035 M	132°C	20 ± 1 %
6. chlorobenzene with K <sub>2</sub> CO <sub>3</sub>	.036 M	132°C	9 ± 2 %
7. water/ethanol 1:2 by volume	.04 M	80°C	6 ± 2 %



has a wavelength of maximum absorption at 289 nm with an absorptivity coefficient of  $\log \epsilon = 3.4$ . The absorptivity coefficients of both product and reactant are close enough so that absorbances at both 268 and 289 nm could be monitored without dilution. In addition to the absorption maxima at 289 nm, which was at least partly due to phenoxide, the decomposition of O-(phenyl)hydroxylamine under all conditions gave another wavelength of maximum absorption between 312 and 318 nm. (Figure 1)

O-(p-nitrophenyl)hydroxylamine absorbs at 315 nm with  $\log \epsilon = 3.36$  while p-nitrophenoxide absorbs at 400 nm with  $\log \epsilon = 4.26^{17}$ , so this reaction could also be monitored by UV absorption spectroscopy, without dilution. During the decomposition of O-(p-nitrophenyl)hydroxylamine an absorption maxima appeared at 400 nm while the absorption maxima at 315, due to reactant, gradually disappeared. After five hrs, however, the peak at 400 nm began to disappear and the absorbance at 315 nm increased. No other peaks of maximum absorption appeared throughout the course of the reaction. (Figure 2)

1. Decomposition of O-(phenyl)hydroxylamine: For each decomposition of O-(phenyl)hydroxylamine in water, the absorbance at 268, 289 and 318 nm was tabulated. A plot of  $\log(a_0 - a_\infty)/(a_t - a_\infty)$  vs time or a plot of  $1/(a_t - a_\infty)$  vs time was prepared to determine the kinetics of product formation. A summary of the results, at the different wavelengths is given in Table 5. A rate constant for the reaction



Figure 1

Absorbance During Decomposition of O-(Phenyl)hydroxylamine

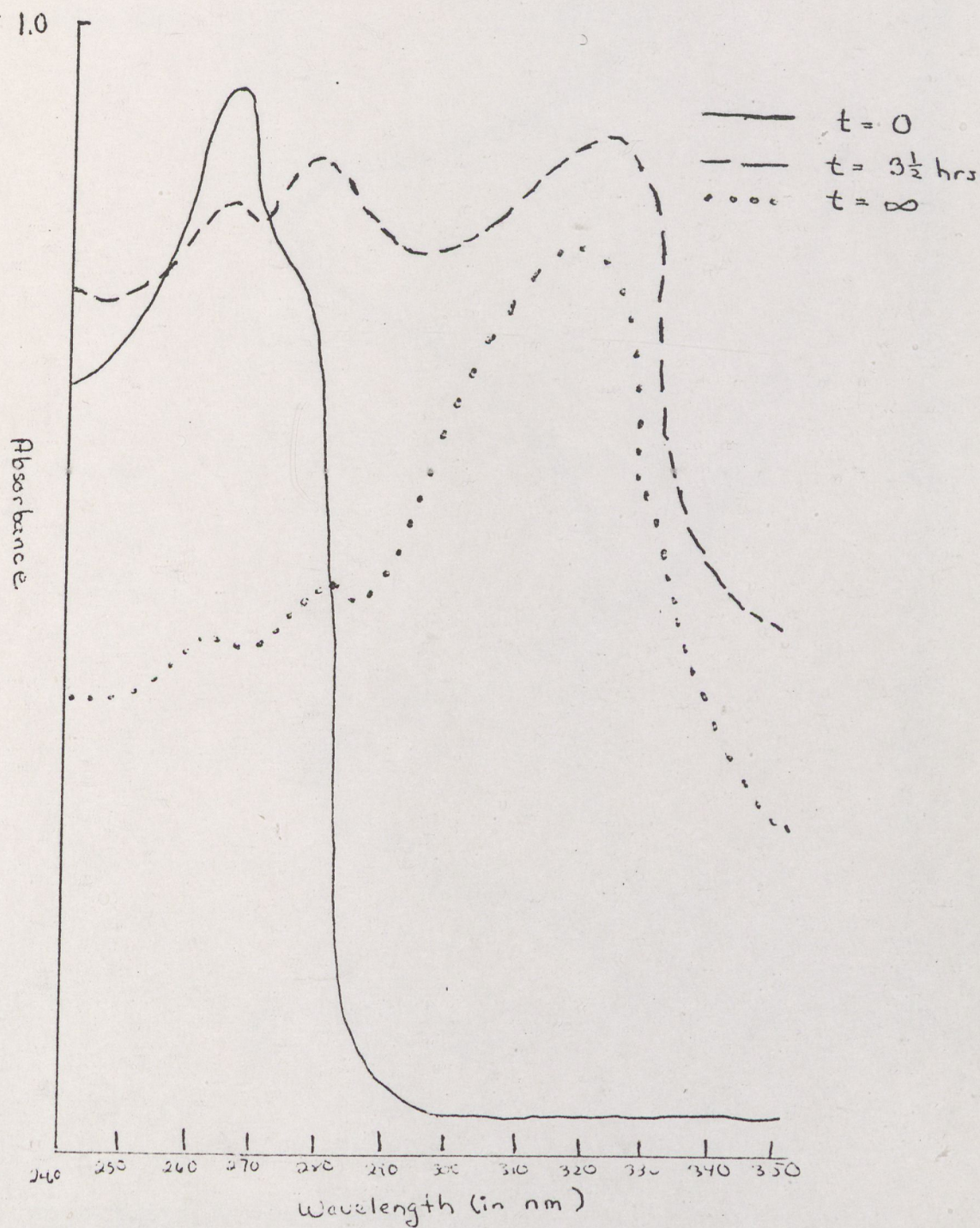
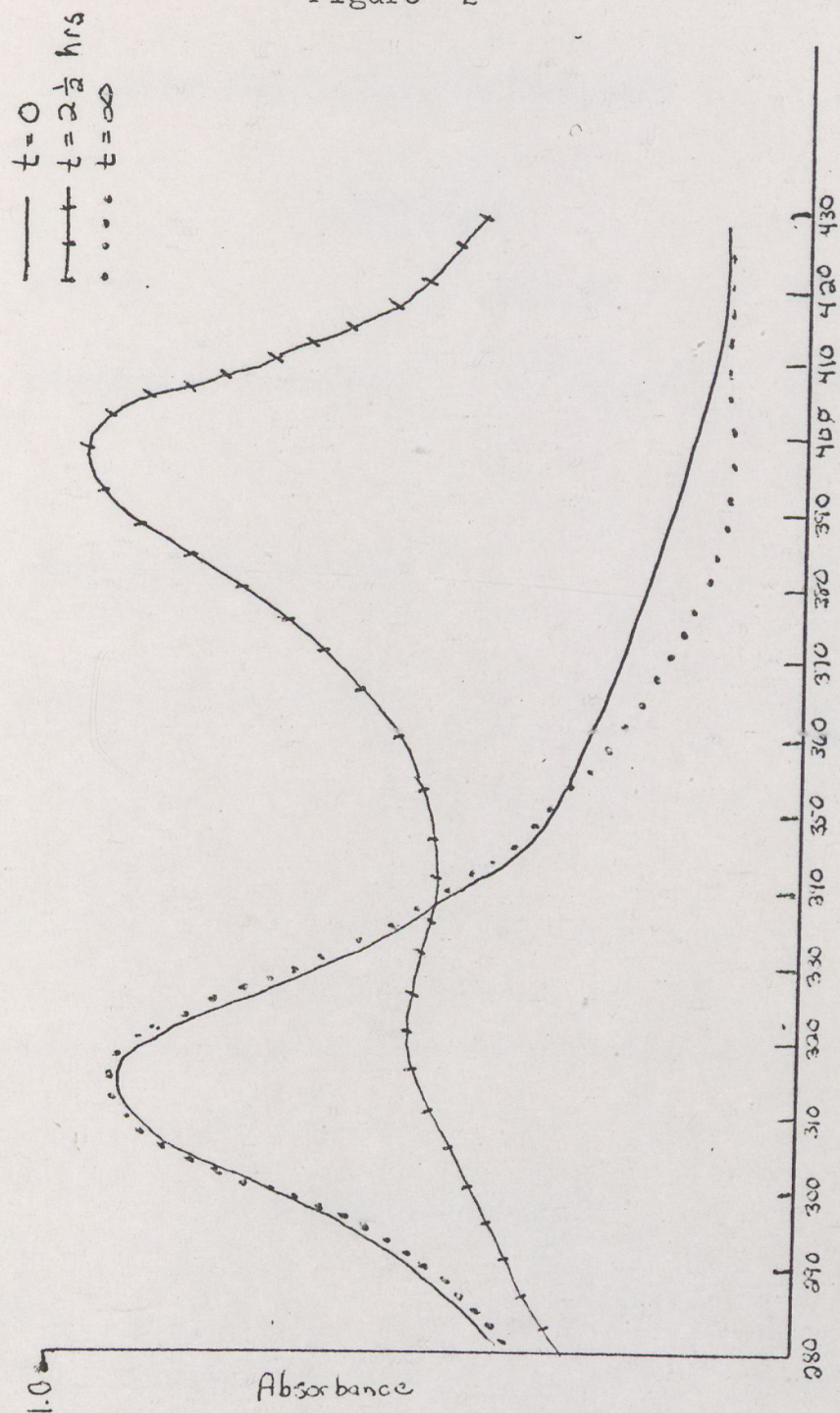




Figure 2



Absorbance During Decomposition of C-(p-Nitrophenyl)

hydroxylamine



Table 5

Kinetics of Product Formation

<u>Reaction</u> *	<u>Wavelength</u>		
	<u>268 nm</u>	<u>289 nm</u>	<u>318 nm</u>
1	absorption increases	1 <sup>st</sup> order	1 <sup>st</sup> order
2	"	"	"
3	"	"	"
4	absorption decreases	"	"
5	"	"	"
6	absorption increases	"	neither 1 <sup>st</sup> or 2 <sup>nd</sup> order
7	"	"	"
8	"	"	"
9	"	"	"

\* Reaction Conditions

	$\left[ \text{C}_6\text{H}_5\text{NH}_2 \right]$	$\left[ \text{CO}_3^{2-} \right]$	$\left[ \text{C}_6\text{H}_5\text{NH}_2 \right]$	$\left[ \text{OH}^- \right]$
1.	$8.0 \times 10^{-4} \text{ M}$	$8.0 \times 10^{-4} \text{ M}$	6. $8.10 \times 10^{-4} \text{ M}$	$4.0 \times 10^{-4} \text{ M}$
2.	$3.8 \times 10^{-4} \text{ M}$	$3.8 \times 10^{-4} \text{ M}$	7. $8.0 \times 10^{-4} \text{ M}$	$8.0 \times 10^{-4} \text{ M}$
3.	$1.5 \times 10^{-3} \text{ M}$	$1.5 \times 10^{-3} \text{ M}$	8. $8.0 \times 10^{-4} \text{ M}$	$16.0 \times 10^{-4} \text{ M}$
4.	$8.0 \times 10^{-4} \text{ M}$	$3.2 \times 10^{-4} \text{ M}$	9. $8.0 \times 10^{-4} \text{ M}$	$8.0 \times 10^{-3} \text{ M}$
5.	$8.0 \times 10^{-4} \text{ M}$	$6.4 \times 10^{-4} \text{ M}$		



was calculated from plots that indicated first order kinetics. Two sample plots of  $\log(a_0 - \infty)/(a_t - \infty)$  vs time are given in Figs. 3 and 4. The initial slopes of the lines, multiplied by 2.3, give the rate constants tabulated in Table 6.

The rate constants calculated from the absorbance at 289 nm, for all the reactions except the one using .0008 M O-(phenyl)hydroxylamine in the presence of .00034 M carbonate and for the decomposition in ethanol/water are assumed to be the same. The value for the reaction of .0008 M O-(phenyl)-hydroxylamine and .0016 M hydroxide is believed to be erroneous, considering the agreement between the other three rate constants for the reactions with varied concentration of hydroxide. Thus, the rate of reaction does not vary with concentration of starting material or concentration of hydroxide ion present.

The rate of reaction also does not vary with the presence of carbonate, as long as a minimum amount is present. The decomposition in the presence of bicarbonate occurred both at a lower temperature and in a different solvent system than the other reactions, so it is not possible to compare the effect of bicarbonate vs carbonate or hydroxide on the decomposition.

At 318 nm the rate constants for the reaction of .0008 M O-(phenyl)hydroxylamine with .00032, .00064 and .0008 M carbonate are all in agreement. The rate constant calculated from the absorbance at this wavelength, however, increases



Figure 3

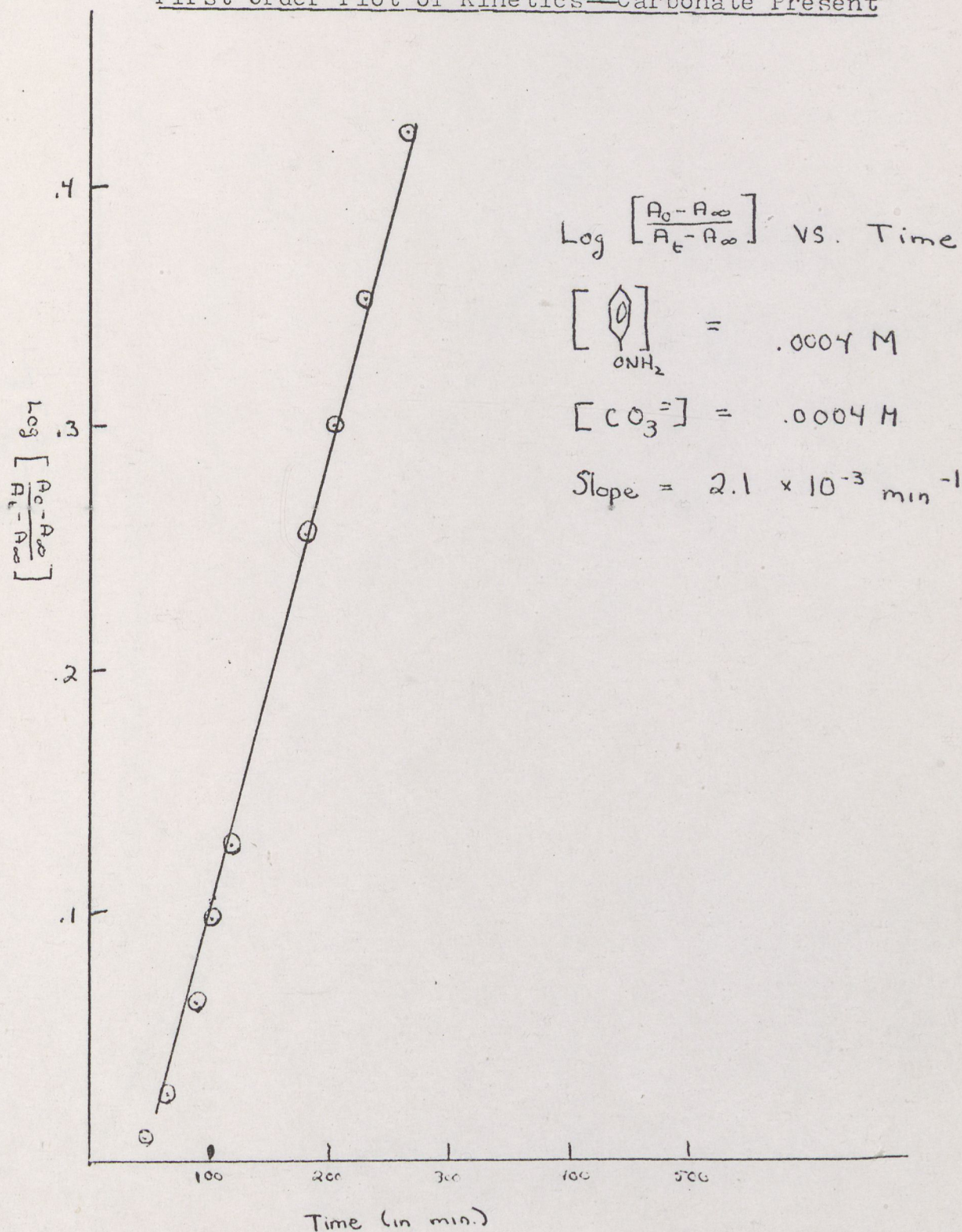
First Order Plot of Kinetics—Carbonate Present



Figure 4

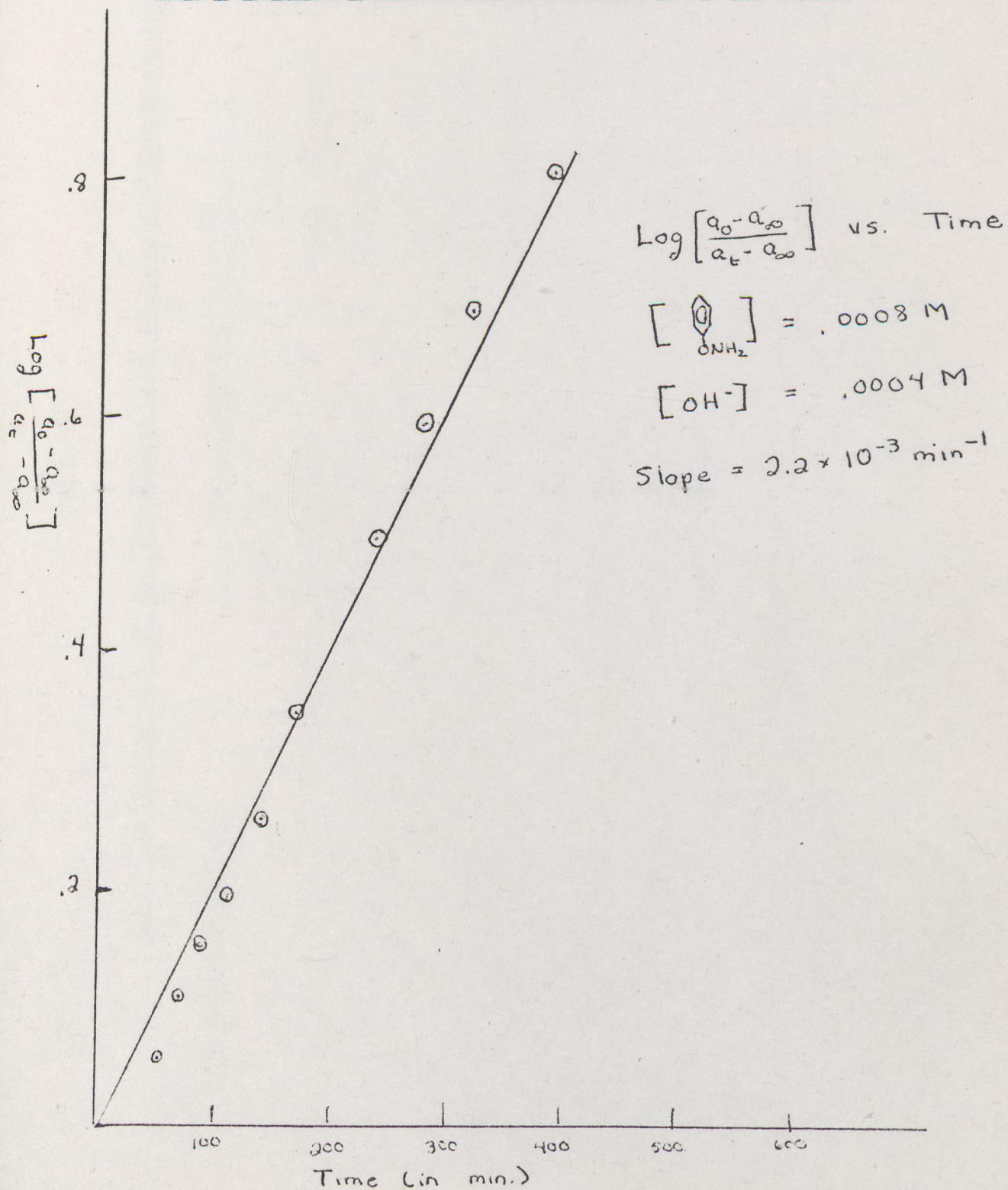
First Order Plot of Kinetics—Hydroxide Present



Table 6

Rate Constants and pH for Decomposition of O-(phenyl)hydroxylamine

<u>Reaction Conditions</u> <sup>*</sup>	<u>Rate Constant (min<sup>-1</sup>)</u>		<u>pH</u>
	<u>289 nm</u>	<u>318 nm</u>	
1	.0046 ± .0008	.0022 ± .0002	10.3
2	.0047 ± .0008	.0020 ± .0002	10.3
3	.0048 ± .0008	.0064 ± .0003	10.3
4	.0030 ± .0002	.0022 ± .0002	9.9
5	.0055 ± .0003	.0022 ± .0002	10.2
6	.0051 ± .0008	.00	10.6
7	.0058 ± .0005		10.9
8	.0030 ± .0003		11.2
9	.0055 ± .0008		11.9

See Table 5



with increased concentration of O-(phenyl)hydroxylamine. When hydroxide ion is present, the reaction can not be described by either first or second order kinetics.

For all the reactions except those in the presence of the two lower concentrations of carbonate, the absorbance at 268 nm eventually increases, indicating that as decomposition proceeds, the absorbance at this wavelength is due to some species besides starting material.

## 2. Decomposition of O-(p-nitrophenyl)hydroxylamine:

Although the absorbance at the wavelength of maximum absorption of p-nitrophenoxide eventually disappeared towards the end of the reaction, a plot of  $\log(a_0 - a_\infty)/(a_t - a_\infty)$  vs time was prepared for the initial part of the decomposition, giving a first order rate constant of  $0.39 \pm .01 \text{ min}^{-1}$ .

## Effect of pH on the rate of decomposition of O-(phenyl)hydroxylamine

For each of the decompositions of O-(phenyl)hydroxylamine in water the pH of the solution at the beginning of the reaction was calculated. The solutions that contained carbonate were treated as buffers and the pH was calculated using the following equation:

$$\text{pH} = -\log \frac{(\text{acid})}{(\text{anion})} K_a$$

The concentration of acid was set equal to the concentration of bicarbonate formed by treating O-(phenyl)hydroxylamine hydrochloride with potassium carbonate to give the



O-(phenyl)hydroxylamine. The value of the acid dissociation constant of bicarbonate is  $5.6 \times 10^{-11}$ . Although another base, O-(phenyl)hydroxylamine is present in the solution it is weakly basic ( $K_b = 1.07 \times 10^{-8}$ )<sup>18</sup> and is not expected to affect the pH of the solution. The values of pH for each of the decompositions are tabulated in Table 6. A dependence of reaction rate on the pH of the solution was not found.

#### Spectral analysis of decomposition products

NMR spectra of the decomposition products of O-(phenyl)-hydroxylamine in decane and chlorobenzene were taken. Shift positions and integrations of the peaks are given in Tables 7 and 8. A spectrum of aniline in chlorobenzene, taken for comparison purposes has a sharp singlet at 3.3 ppm, suggesting the presence of an amino group on the products of the decomposition. An IR spectrum of the decomposition products in decane was also taken. Only two peaks not attributable to the solvent were found:

broad band	3650 - 3100 $\text{cm}^{-1}$
medium broad band	1640 $\text{cm}^{-1}$

An IR spectrum of a suspension of phenol in decane gave a very broad band in the 3500-3100  $\text{cm}^{-1}$  range.

The presence of  $\text{NH}_2$  and OH groups on the product compounds is indicated, perhaps in the form of aminophenols.

The final concentrations of phenoxide that could have been formed during the decomposition of O-(phenyl)hydroxyl-



Table 7

NMR Spectra of Decomposition Products in Decane

<u>Sample</u>	<u>Position (ppm)</u>	<u>Integration</u>
Starting material	singlet at 7.0	41
	broad multiplet at 6.5-7.0	
	broad singlet at 5.5	16
After heating one minute	singlet at 7.0	35
	broad multiplet at 6.5-7.0	
	broad singlet at 5.4	12
After heating five minutes	singlet at 7.0	35
	sharper multiplet at 6.5-7.0	
	very broad peak at 5.4	10
After decomposition	triplet at 7.1	
	doublet at 6.8	



Table 8

NMR Spectra of Decomposition Products in Chlorobenzene

<u>Sample</u>	<u>Position (ppm)</u>
Starting material	broad band at 5.4
After heating four minutes	"
After heating nine minutes	"
After heating nineteen minutes	no peak
After decomposition	sharp singlet at 3.3



amine were calculated for several of the reactions from the values of  $a$  at 289 nm. These values range broadly and in some instances are slightly higher than the initial concentration of O-(phebyl)hydroxylamine. The concentration and percent yield of phenoxide for the reactions are tabulated in Table 9; the average yield of phenoxide was 84%.



Table 9

Yield of Phenoxide as Calculated From  $a_{\infty}$  at 289 nm

<u>Reaction</u> <sup>*</sup>	<u>Concentration of Phenoxide</u>	<u>% Yield</u>
1	$7.9 \times 10^{-4}$ M	99
2	$4.7 \times 10^{-4}$ M	87
3	$1.3 \times 10^{-3}$ M	124
4	$3.6 \times 10^{-4}$ M	45
5	$3.9 \times 10^{-4}$ M	49
6	$4.8 \times 10^{-4}$ M	66
7	$5.8 \times 10^{-4}$ M	73
8	$1.1 \times 10^{-3}$ M	138
9	$6.3 \times 10^{-4}$ M	79

\* See Table 5

Average Yield = 84 %



## DISCUSSION



Synthesis of O-(phenyl)hydroxylamine

According to the model studies performed by R. Sommers<sup>12</sup> the synthesis of an O-substituted hydroxylamine compound from a halobenzene and hydroxylamine should be maximized under basic conditions, where the nucleophile is presumably  $\text{NH}_2\text{O}^-$ . In the reactions of the p-nitrohalobenzenes with hydroxylamine, hydrogen chloride is liberated. To insure that the desired basic conditions of the reaction were maintained, twice as much hydroxylamine as the benzene compound was used in each reaction. The extra hydroxylamine acts as a base, removing excess hydrogen ions from the solution.

In the reactions using the hydroxylamine solution with 10% excess base, methoxide ion was present. Attack at the benzene ring by this nucleophile, however, did not occur as shown by the NMR spectra of the recovered neutral materials for each reaction. The recovery of starting material (from 86-94%) and the absence of any p-nitroanisole in the reaction mixtures indicates that the reaction conditions were not strenuous enough.

The validity of applying reaction conditions that maximize an  $\text{S}_{\text{N}}2$  reaction to a reaction involving an  $\text{S}_{\text{N}}\text{Ar}$  mechanism seems suspect. The model studies involving the reaction of benzyl chloride with hydroxylamine were performed at room temperature for 20 hrs. With the model study using p-nitrochlorobenzene and methoxide ion, however, the reaction mixture had to be refluxed for 24 hrs before complete formation



of p-nitroanisole occurred.

Aromatic rings are much less susceptible to nucleophilic attack than are compounds which react through an  $S_N2$  mechanism. The  $sp^2$  hybridized carbon is much more electronegative than the  $sp^3$  hybridized carbon and it does not allow the leaving group to depart with its extra electrons as easily. In addition, resonance between a leaving group that has extra electrons and an aromatic ring stabilizes the molecule and decreases the rate of nucleophilic attack. The more vigorous conditions required for an  $S_NAr$  attack by a nucleophile are most likely detrimental to the already unstable O-substituted phenylhydroxylamine compound.

The formation of O-(phenyl)hydroxylamine from the phenolate ion and hydroxylamine-O-sulfonic acid does not involve an  $S_NAr$  mechanism, and thus the conditions needed for reaction are less strenuous; the reaction mixture is refluxed for only ten minutes. The reaction seems to proceed by  $S_N2$  displacement of the sulfate ion at the nitrogen. It is run in an excess of base and the hydroxylamine-O-sulfonic acid is present in the form of its ion,  $NH_2OSO_3^-$ . Krueger et al.<sup>6</sup> find, surprisingly, that the anion is more reactive towards the nucleophile than is the protonated form. It might be expected that the protonated form would be more reactive, since there would be a lower net charge on the activated complex in the transition state.



Also, a protonated nitrogen should be more susceptible to attack by a negatively charged nucleophile.

Water is used as the solvent in the synthesis because of the low solubility of hydroxylamine-O-sulfonic acid in many organic solvents, and to stabilize the sulfate leaving group. The work by Krueger<sup>6</sup> involving  $S_N2$  reactions of hydroxylamine-O-sulfonic acid in solvent systems with different ratios of DMSO to water confirms the assumption that the reaction goes more quickly in the more polar solvent. An organic solvent is used in the synthesis to remove O-(phenyl)hydroxylamine from the water layer. Methylcyclohexane is chosen because its boiling point is so close to that of water's.

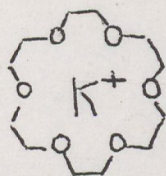
The yield for the synthesis of O-(phenyl)hydroxylamine is quite low (9-18%). This is probably due to the instability of hydroxylamine-O-sulfonic acid in water at room temperature; at reflux, it decomposes rapidly. Balancing the two factors, instability of hydroxylamine-O-sulfonic acid in water and the stabilizing effect of water on the sulfate leaving group, might lead to an improvement in the synthesis. It is thought that the reaction might be more profitably run in a solvent such as dimethylformamide or hexamethylphosphoramide, where instability of hydroxylamine-O-sulfonic acid should not be as much of a problem.

The insolubility of both hydroxylamine-O-sulfonic acid

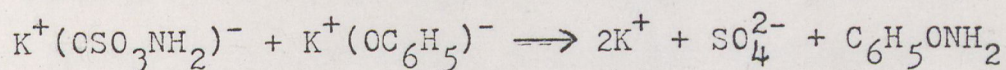


and its potassium salt in these solvents poses a problem, however.

The recent use of crown ethers to complex metal salts might offer a solution to this problem. Liotta and Harris<sup>19</sup> report the use of 18-Crown-6 ether to solubilize potassium fluoride in acetonitrile and benzene. The fluoride ion is able to take part in displacement reactions at both  $sp^2$  and  $sp^3$  hybridized carbon atoms. It might be possible to use 18-Crown-6 ether (below) to complex the potassium ion



in both of the reactants for the synthesis of O-(phenyl)-hydroxylamine, thus increasing their solubilities:



O-(phenyl)hydroxylamine is unstable in air, so it is converted to its hydrochloride salt for storage. The salt is recrystallized from ethyl acetate and much of the product can be lost during recrystallization if hydrogen chloride is not passed through the mother liquor. The hydrochloride salt is also unstable over long periods of time so it is stored in the refrigerator, under nitrogen.

The synthesis of O-(p-nitrophenyl)hydroxylamine also gives a poor yield. The nitrated compound is probably more unstable than O-(phenyl)hydroxylamine because of the presence



of an electron withdrawing group on the ring.

### Product analysis

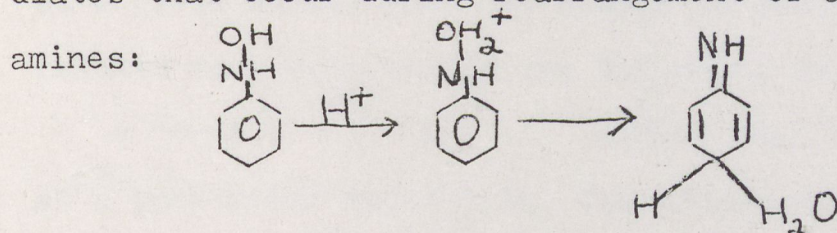
Although it was not possible to identify the product from the reaction of hydroxylamine and p-nitrofluorobenzene it is unlikely that the product contains the desired O-(p-nitrophenyl)hydroxylamine. The product has an absorption maxima at 356 nm, while O-(p-nitrophenyl)hydroxylamine has a maxima at 315 nm. The absorption maxima does agree with the maxima for the N-substituted (p-nitrophenyl)hydroxylamine (356 nm).<sup>17</sup> The melting point of the product (183-185°C) however does not agree with that of N-(p-nitrophenyl)hydroxylamine which melts at 107°C<sup>20</sup> when recrystallized from benzene.

Several other possibilities of products that might have been formed were considered. A good NMR spectrum of the compound was difficult to obtain because of its low solubility in chloroform, carbon tetrachloride, acid solution and acetone. The compound was slightly soluble in dimethyl sulfoxide and its NMR spectrum shows peaks at 8.4 and 7.6 ppm, with areas in the ratio of 3:2. Shaking the mixture with D<sub>2</sub>O reduced the area under the peak at 8.4 ppm. The NMR data refutes any aminophenol products that could have been formed by attack of hydroxylamine at the ring, with subsequent rearrangement. Protons ortho to the nitro group should occur furthest downfield and when amino and hydroxyl groups are present



on the ring, they should give peaks occurring below 8.2 ppm. Although both 2-amino,4-nitrophenol and 5-amino,4-nitrophenol have melting points that agree with the product, ref.<sup>20</sup> 195-8d and 185-6d, respectively, their structures do not agree with the NMR data.

It was also not possible to identify the compounds producing the red colors during the work-up procedure. Not enough product was present in the solution to isolate. One possibility is that these compounds are Meisenheimer Salt type intermediates where two nucleophiles are attached at the same position and the nitro group helps bear the excess negative charge. Another possibility to be considered are the intermediates that occur during rearrangement of aryl hydroxylamines:



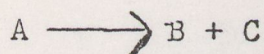
Compounds similar to III have been isolated when the para position is blocked.<sup>21</sup> Finally, the bright red colors of the reaction solutions make compounds resulting from the oxidative coupling reactions of phenols likely possibilities.

### Kinetics

For first order reactions, a plot of  $\log[A]_t/[A]_0$  vs time will give a slope equal to  $k/2.3$ , where A is a reactant and



and  $k$  is a rate constant. In the reaction below, the concen-



tration of A can be found from the concentration of either B or C. When one of the species involved in a reaction absorbs in the ultraviolet range, UV absorption spectroscopy provides a convenient method for following the change in concentration of reactants or products. Absorbance at the wavelength of maximum absorption is related to concentration by Beer's Law:

$$A = abc$$

A = absorbance  
a = absorptivity coefficient  
b = cell path length  
c = concentration

When more than one of the species in a reaction absorbs at a given wavelength, the change in concentration of A is related to absorbance in the following manner:

$A \longrightarrow B + C + D + \dots$  Assume that both A and B absorb at a particular wavelength. The absorbance at that wavelength is due to the combined absorbances of B and C present in the solution.

Let  $\alpha$  = fraction of A going to B

Let  $\beta$  = fraction of A going to C

The concentrations of B and C are related to the concentration of A by  $\alpha [A]^0 = [B]_{\infty}$  and at time  $t$  by  $\beta [A]^0 = [C]_{\infty}$

$$[A]^t = [A]^0 - \frac{[B]^t}{\alpha} \quad \text{and} \quad [A]^t = [A]^0 - \frac{[C]^t}{\beta}$$

Thus the absorbance at time  $t$  is given by:



$$\begin{aligned}
 A^t &= A_B^t + A_C^t & A_B &= a_B b [B] & A_C &= a_C b [C] \\
 &= (a_B b [B]^t + a_C b [C]^t) & b &= 1 \text{ cm} \\
 &= (a_B ([A]^0 - [A]^t) + a_C ([A]^0 - [A]^t)) \\
 &= ([A]^0 (\alpha a_B + \beta a_C) - [A]^t (\alpha a_B + \beta a_C)) \\
 &= [A]^\infty - [A]^t (\alpha a_B + \beta a_C)
 \end{aligned}$$

$$\frac{A^t - A_\infty}{\alpha a_B + \beta a_C} = -[A]^t$$

$$A_\infty = [A]^0 (\alpha a_B + \beta a_C)$$

$$[A]^0 = \frac{A_\infty}{\alpha a_B + \beta a_C} \quad \text{and}$$

$$\frac{[A]^t}{[A]^0} = \frac{A_t - A_\infty}{-A_\infty}$$

$$\frac{A_t - A_\infty}{-A_\infty} = e^{-kt}$$

$$\frac{\log(A_t - A_\infty)}{(-A_\infty)} = \frac{kt}{2.3}$$

If A initially absorbs at the same wavelength that B and C absorb, then

$$\frac{\log(A_t - A_\infty)}{(A_0 - A_\infty)} = kt / 2.3$$

For the decomposition of O-(phenyl)hydroxylamine, one of the products, phenoxide, absorbs at 289 nm. From the values of absorbance at 289 nm at infinite time, the concentration of phenoxide present was calculated. Since these values are in some cases higher than the initial concentration of O-(phenyl)hydroxylamine, it is likely that evaporation of the solution occurred since it refluxed overnight, or that some product besides phenoxide absorbs at 289 nm. The plots



of  $\log(a_0 - a_\infty)/(a_t - a_\infty)$  vs time for  $\lambda$  at 289 nm, give straight lines and therefore indicate that phenoxide and possibly some other product are produced by a 1<sup>st</sup> order reaction.

At least one additional product that absorbs at 312-318 nm is produced in all cases, either by a first order mechanism when carbonate is present or by a higher order mechanism in the presence of hydroxide.

In the decomposition of O-(p-nitrophenyl)hydroxylamine it appears that p-nitrophenoxide is initially produced by a first order mechanism, but that it subsequently goes on to form other products.

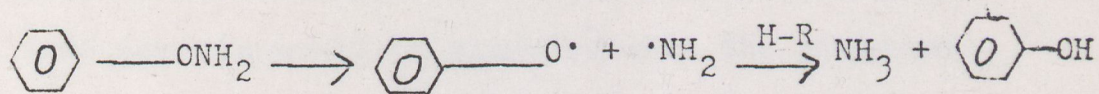
#### Mechanism of the reaction

The calculated values of  $\Delta H$  for the dissociation of hydroxylamine and its methylated derivatives into radicals and ions indicate that dissociation into radicals is favored. Although the MINDO/3 program<sup>15</sup> is not capable of treating the p-p repulsions found in a molecule like hydroxylamine the differences in the heats of reaction for the two paths are large enough to suggest that O-(phenyl)hydroxylamine should decompose most easily into radicals in organic solvents.

In the decompositions run in organic solvents, the production of basic gas helps support the idea of dissociation into radicals. The basic gas is assumed to be ammonia, which could easily be produced by the reaction of an imino

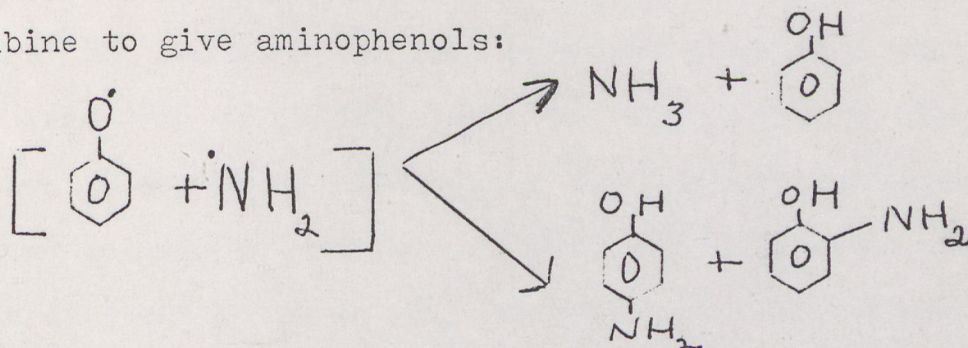


radical with hydrogen atoms bound to the solvent, or to other species in solution:



Similarly, the phenoxy radicals could abstract H atoms to give the phenol that is suggested by the IR spectrum of the reaction products in decane.

Some of the additional data available indicate that the reaction is more complicated than just dissociation into radicals that abstract hydrogen atoms to give ammonia and phenol. The NMR spectrum of the reaction products in chlorobenzene indicates that an amine of some sort is formed, most probably an aminophenol. This suggests that after dissociation, at least two different pathways are possible for further reactions of the radicals. A likely possibility is that the radicals, upon formation, are held in a solvent cage from which they can diffuse and abstract hydrogen atoms or can combine to give aminophenols:



The fraction of radicals that go on to form ammonia is the same for the reaction in three different solvents and does not depend on the concentration of the starting material. This rules out the production of aminophenols by an induced



radical mechanism involving attack by  $\cdot\text{NH}_2$  on the starting material. With this type of mechanism, more aminophenol and less ammonia would be expected when the reaction was run at higher concentrations of O-(phenyl)hydroxylamine.

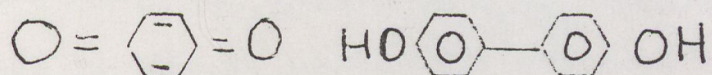
The fact that the amount of ammonia produced does not depend on the solvent is surprising, particularly if the production of ammonia is controlled by the rate of diffusion of radicals from a solvent cage. The rate of diffusion should depend on the viscosity of the medium. However decane and chlorobenzene at least, have similar viscosities at room temperature (decane .92 cp, chlorobenzene .8 cp)<sup>20</sup> and at the boiling points of these solvents their viscosities may be essentially the same. A repetition of the decomposition experiment in solvents that do differ markedly in viscosity could give definite information about the possibility of diffusion occurring from a solvent cage.

When considering the possibility of a radical mechanism, where  $\cdot\text{NH}_2$  radicals abstract hydrogen atoms from the solvent, the fact that no dicumyl could be recovered from the decomposition in cumene is disturbing. The tertiary hydrogen on cumene is easily lost as a radical and when other compounds such as diacetyl peroxide,<sup>22</sup> decompose by radical mechanisms in cumene, pure dicumyl can be recovered as a white solid, m.p. 115°C. Perhaps either dicumyl was present in the brown solid that was recovered upon work-up of the cumene or abstraction of hydrogen atoms from the solvent did not occur.



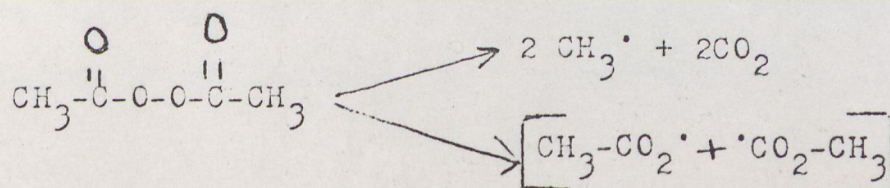
The latter possibility is unlikely, since the decomposition solutions are dilute and the amount of ammonia formed does not depend on the concentration of starting material. The solvent, present in large excess, is the most likely site of hydrogen abstraction.

In addition to ammonia and aminophenols it is likely that some other products are formed during the decomposition of O-(phenyl)hydroxylamine. The reaction solutions turned dark red and then black during the course of the decomposition. The most likely compounds causing the changes in color are quinones and coupled products resulting from oxidative reactions of the phenoxy radical:



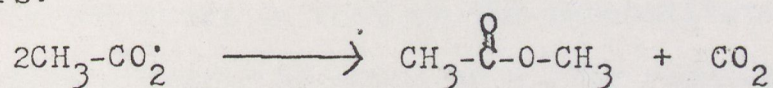
Phenol is well-known for its ability to inhibit radical reactions and form the above types of compounds.

Additional evidence for a radical mechanism for the decomposition of O-(phenyl)hydroxylamine comes from a comparison of the compound with related peroxides. Compounds of the type RO-OR undergo both induced decomposition and simple dissociation into  $\cdot\text{OR}$  radicals.<sup>23</sup> Evidence for a solvent cage type of reaction is also found in the reactions of peroxides. Diacetyl peroxide decomposes into carbon dioxide, methane and ester:





80 % carbon dioxide is formed during the course of the reaction. A 20% yield of ester is also produced and it is suggested<sup>23</sup> that the ester is formed through a solvent cage intermediate. The two acetoxy radicals are held closely together by solvent molecules where they can react to give esters:



The ratio of carbon dioxide produced does not change when a radical inhibitor is added. Formation of the ester is not affected by the presence of a radical inhibitor because the acetoxy radicals react before leaving the cage. Compounds with an O-N bond might be expected to act like ~~these~~ with an O-C bond, due to similar  $\underset{\pi}{\text{p}}\text{-}\underset{\pi}{\text{p}}$  repulsions in the molecules.

It is hard to account for the amount of ammonia produced during the decomposition in chlorobenzene, with carbonate present. Perhaps the carbonate serves to remove some source of  $\cdot\text{NH}_2$  radicals by means of an acid-base reaction or by a reaction with an amino group.

Although the decomposition into radicals is favored thermodynamically and seems the likely mode for reaction in organic solvents, much evidence exists for the operation of another mechanism in the decompositions that took place in water. The calculated heats of reaction indicate that dissociation into radicals is favored over dissociation into ions. The heat of formation values, however, were calculated for the equivalent of a gas phase reaction. Disso-



ciation into ions should be stabilized in polar solvents such as water, perhaps to the extent that this reaction competes with the formation of radicals.

The difference in rate constants for the decomposition of O-(phenyl)hydroxylamine and O-(p-nitrophenyl)hydroxylamine is important here. The nitrated compound decomposed nearly ten times as fast as the unsubstituted compound. An electron withdrawing group on a ring reduces the rate of radical formation at the  $\alpha$  position to the ring<sup>24</sup> so addition of a nitro group would be expected to decrease the rate of decomposition if it is occurring by a radical mechanism. However, if decomposition occurs by way of an ionic mechanism, the presence of a nitro group explains the increase in rate. An electron withdrawing group can delocalize the charge on a phenoxide ion, thus stabilizing the leaving group and making decomposition more likely.

Although the production of ammonia is decreased in the nucleophilic solvent, 6% ammonia is still obtained. This, and the fact that decomposition into radicals is favored thermodynamically, suggests that two mechanisms may be operating at the same time. A radical mechanism, producing ammonia may compete with an ionic mechanism that is responsible, at least partly, for the production of phenoxide in the reaction mixture. If the differences in the rate constants for the unsubstituted and the nitrated compounds are considered, it is realized that the predominant reaction



in water must be of an ionic type. The mechanism is described by a first order rate constant. If this rate constant describes two simultaneous reactions the greater contribution must come from a reaction that is more favored by the presence of a nitro group on the ring. As discussed, only the ionic reaction is expected to go faster and this reaction must give the larger contribution to the rate constant.

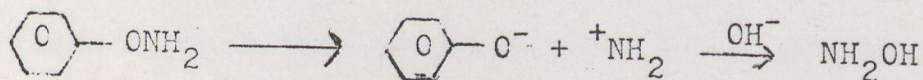
Additional evidence for the operation of more than one mechanism comes from the changes in absorbance with time at 268 nm. The reactant absorbs in this region and if the only reaction occurring was a straightforward substitution reaction producing phenoxide, the absorbance in this area would be expected to decrease as reactant was consumed. However, for all the reactions except the two with the lowest concentration of base, the absorbance initially decreases and then increases. This is best explained by an initial decomposition of  $\text{O}-(\text{phenyl})\text{hydroxylamine}$  to give a decrease in absorbance, followed by the production of a species that absorbs in the region from 260-285 nm. The anions of the aminophenols already introduced to explain the IR and NMR spectra also absorb from 280-295 nm, depending on the concentration of base present in the solution. This supports the idea that the radical mechanism proposed for the decomposition in organic solvents may also be operating in the decomposition in water.

Further support for the ionic pathway is the yield of



phenoxide, as calculated from values of absorbance at infinite time for each of the decompositions in water. Although the individual values vary, the average yield is 84%, indicating that an ionic mechanism, producing phenoxide, must dominate.

The rate constants and the reaction order for the decompositions in water are in accord with both a radical and an ionic mechanism. The production of phenoxide is governed by a first order mechanism, indicating that an  $S_N1$  reaction, rather than an  $S_N2$  reaction may be occurring. The rate determining step in an  $S_N1$  reaction involves only the dissociation of O-(phenyl)hydroxylamine and should give a first order rate expression:



With an  $S_N2$  reaction, however, the nucleophile is involved in the rate determining step and the reaction is second order.

Decomposition into radicals, which may also be contributing to the rate constant, should also be first order. The radicals formed are probably held in a solvent cage and should recombine quickly so that the rate of reaction depends only on the initial decomposition step, giving a first order expression that depends only on the concentration of the starting material.

The fact that the rate law does not depend on either



the initial concentration of starting material or on the concentration of base present also supports the first order  $S_N1$  mechanism. Only the reaction with the lowest concentration of base gave a different rate constant. The amount of phenoxide produced in this reaction was only about half of that possible based on the initial concentration of the starting material. Perhaps there was insufficient base present to convert any phenol produced to its anion.

The kinetics for the decomposition of O-(p-nitrophenyl)-hydroxylamine also give a first order rate expression for the initial part of the reaction. Phenoxide starts to disappear with time however, and its maximum concentration ( $5.0 \times 10^{-5} M$ ) is only a fourth of that possible. p-Nitrophenoxide may be initially produced in a reaction similar to that of the unsubstituted compound, but an additional reaction that begins as p-nitrophenoxide accumulates is probably involved here.

The relatively large rate constant ( $.039 \text{ min}^{-1}$ ) for the decomposition of O-(p-nitrophenyl)hydroxylamine indicates why its synthesis from p-nitrofluorobenzene and hydroxylamine was not successful. The half life for the decomposition is only 18 min., so any O-(p-nitrophenyl)hydroxylamine formed would have decomposed under the reaction conditions since the solutions were refluxed overnight.



## CONCLUSION



It is suggested that O-(phenyl)hydroxylamine decomposes in a manner analogous to the reactions of peroxides, via a radical mechanism in organic solvents. The initial step is probably a unimolecular decomposition into imino and phenoxy radicals, which are held in a solvent cage intermediate. Two pathways are available to the radicals. 80% seem to recombine to give aminophenols while the other 20 % diffuse out of the cage and abstract hydrogen atoms from the solvent to give ammonia and phenol. The phenols may go on and react with radicals in the solution to give oxidative coupling products.

In the nucleophilic solvent, it is suggested that two pathways compete in the decomposition of O-(phenyl)hydroxylamine. Along with the radical mechanism described above, an  $S_N1$  mechanism may operate. The reaction gives first order kinetics and is independent of the initial concentration of starting material or the concentration of nucleophile, as long as a minimum amount of base is present in the solution.

Further work should concentrate on product studies of the reaction, particularly to determine if aminophenols are actually present. Running the reaction in different solvents may give information about a possible solvent cage intermediate since the amount of ammonia produced should be related to the viscosity of the medium. The reaction in nucleophilic solvents should be repeated, varying the



type of substitution on the ring and the nucleophile used. Finally, the reaction should be repeated at higher concentrations of hydroxide to see if there is evidence for the  $S_N2$  mechanism reported by earlier workers.



APPENDIX I



Spectral Data

IR spectra were run on a Perkin Elmer 237 Recording Infrared Spectrophotometer. NMR spectra were run on a Perkin Elmer R-24A High Resolution NMR Spectrometer.

- Spectrum 1: p-nitrochlorobenzene, starting material.
- Spectrum 2: p-nitrochlorobenzene and p-nitroanisole, starting material and product from reaction of p-nitrochlorobenzene and methoxide. The reaction is 60 % complete.
- Spectrum 3: p-nitroanisole, from p-nitrochlorobenzene and methoxide.
- Spectrum 4: p-nitrochlorobenzene, recovered starting material from the reaction of p-nitrochlorobenzene and hydroxylamine.
- Spectrum 5: p-nitrofluorobenzene, starting material. The peaks, due to the ring protons, are split by fluorine.
- Spectrum 6: p-nitrofluorobenzene, recovered starting material from the reaction of p-nitrofluorobenzene and hydroxylamine in excess base.
- Spectrum 7: unidentified product, from the reaction of p-nitrofluorobenzene and hydroxylamine in excess base.
- Spectrum 8: UV spectra of water/methanol layer and acid  
+ 9:



extract layer, following work-up of p-nitrofluorobenzene and hydroxylamine reaction solution. See Table 2.

Spectrum 10: unidentified product of the reaction of p-nitrofluorobenzene and hydroxylamine.

Spectrum 11: IR and UV spectra of O-(phenyl)hydroxylamine  
+ 12: hydrochloride. The broad peak at  $3100\text{ cm}^{-1}$ , extending into the C-H stretches of Nujol, is due to asymmetrical and symmetrical stretches of  $\text{NH}_3^+$ . The peaks at  $1575\text{--}1600\text{ cm}^{-1}$  and  $1500\text{ cm}^{-1}$  are due to  $\text{NH}_3^+$  or C-C ring bending.

Spectrum 13: O-(p-nitrophenyl)hydroxylamine. The peaks at  $1350\text{ cm}^{-1}$  and  $1530\text{ cm}^{-1}$  are due to the nitro group.

Spectra 14-  
22: decomposition of O-(p-phenyl)hydroxylamine in decane and chlorobenzene. See Results.

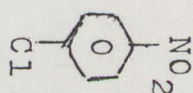
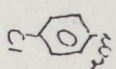
Spectrum 23: aniline in chlorobenzene.

Spectrum 24: decomposition products of O-(phenyl)hydroxylamine in decane.

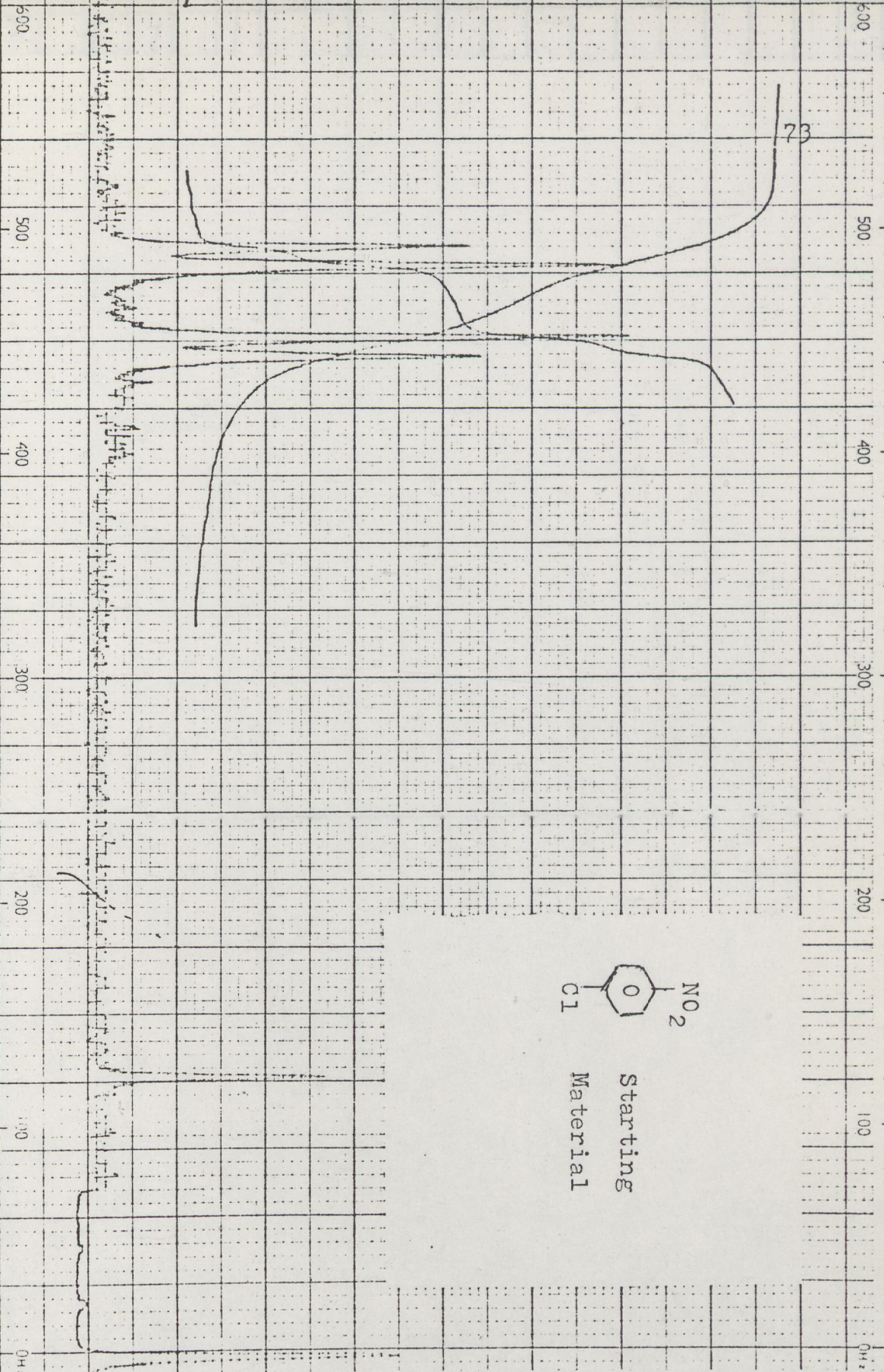


1H SPECTRUM NO.: 7

SAMPLE: .....



Starting  
Material



0.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.1 ppm

+11.3 ppm CF<sub>3</sub>COOH Pyridine(α) Pyridine(γ) Pyridine(β) C<sub>6</sub>H<sub>6</sub>, CHCl<sub>3</sub>

CHO — Ar-H — HC-CH — C-CH<sub>2</sub> — CH<sub>2</sub>Cl<sub>2</sub> — H<sub>2</sub>O — CH<sub>3</sub>OH — p-Dioxane — (CH<sub>3</sub>)<sub>2</sub>SO — (CH<sub>3</sub>)<sub>2</sub>CO — Cyclohexane — TMS

—C-CH<sub>2</sub>-O— —C-CH<sub>2</sub>-N— —CH<sub>3</sub>-CO— —CH<sub>3</sub>-C— —CH<sub>3</sub>-Si—

REMARKS:

acetic anhydride  
at 2 ppm

DATE: 4/14/75

OPERATOR: H. Kennice

SWEEP TIME  
☐ 300.150 SEC ☐

SHIFT

SWEEP WIDTH: SCALE EXP.  
100 200 300 400 500

GAIN: ☐ 10

H<sub>2</sub> LEVEL: ☐ 10

H<sub>1</sub> LEVEL: ☐ 10

AMPLITUDE: X 1.3

SPECTRUM: X 1.3

INTEGRAL: X 1.1

CONC: .....

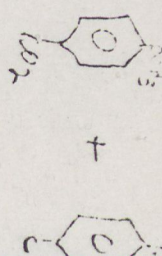
SOLVENT: CCl<sub>4</sub>

REFERENCE: TMS

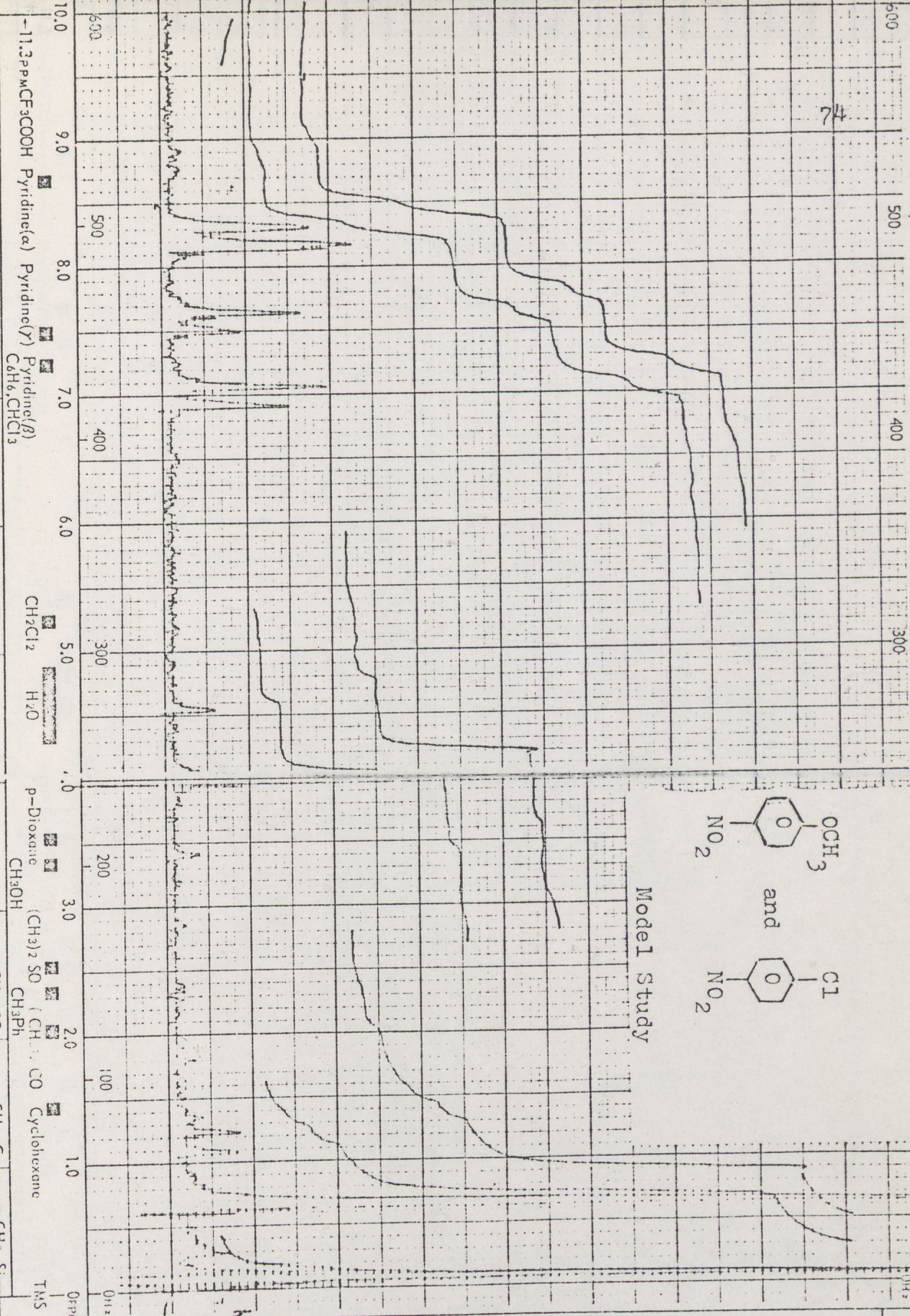
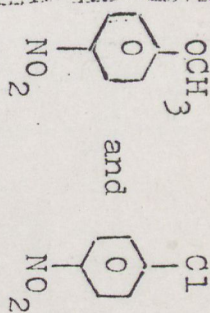


<sup>1</sup>H SPECTRUM NO.: 2

SAMPLE:



# Model Study



REFERENCE: TMS

SOLVENT: CCl4

CONC: 10%

AMPLITUDE: 10

SPECTRUM: 12

INTEGRAL: 1.0

H1 LEVEL:

HI N/A

H2 LEVEL:

GAIN:

X12

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SHIFT 50

DATE: 4/15/75

OPERATOR: L. J. ...

REMARKS:

300.150 SEC

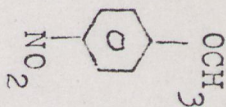
DATE: 4/15/75

OPERATOR: L. J. ...

REMARKS:

-11.3 ppm CF3COOH Pyridine( $\alpha$ ) Pyridine( $\gamma$ ) Pyridine( $\beta$ ) C6H6, CHCl3  
 CHO Ar-H HC-CH C-CH<sub>2</sub> CH<sub>2</sub>Cl<sub>2</sub> H<sub>2</sub>O CH<sub>3</sub>O p-Dioxane (CH<sub>3</sub>)<sub>2</sub>SO (CH<sub>3</sub>)<sub>2</sub>CO Cyclohexane TMS  
 C-CH<sub>2</sub>-O- C-CH<sub>2</sub>-O- CH<sub>3</sub>-CO- CH<sub>3</sub>-N- CH<sub>3</sub>-C- CH<sub>3</sub>-C- CH<sub>3</sub>-Si-





15

2-11-3

SOLVENT: *ethyl*

AMPLITUDE:

INTEGRAL.....

720. X

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	87	88	89	90	91	92	93	94	95	96	97	98	99	100
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NCR  
SCALE EXP.

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☐ 300-150 SEC ☐

OPERATOR 5/5/75

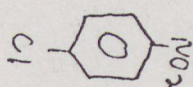
REMARKS:

三

1861



SA 1-1-1



SOLVENT:

CONC:

SPECTRUM.....17

INTEGRAL.....14

100

## GALIN:

XIX

NOR SCALE EXP.

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SHIFT

☐ 300 150 SEC ☐

DATE: 4/26/12

OPERATOR

REMARKS:

1-CH<sub>3</sub> cation base  
Neutral species  
Cc1ccccc1 + NH<sub>4</sub>OH  
U







1H SPECTRUM NO.:

SAMPLE: 15

REFERENCE:  
SOLVENT:  
CONC:

AMPLITUDE:  
SPECTRUM: A 11  
INTEGRAL: 10

H1 LEVEL:

H2 LEVEL:

GAIN:

SWEEP WIDTH:  
SCALE EXP. 100

SHIFT

SWEEP TIME

☐ 300/150 SEC ☐

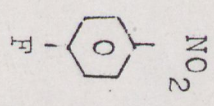
DATE:

OPERATOR

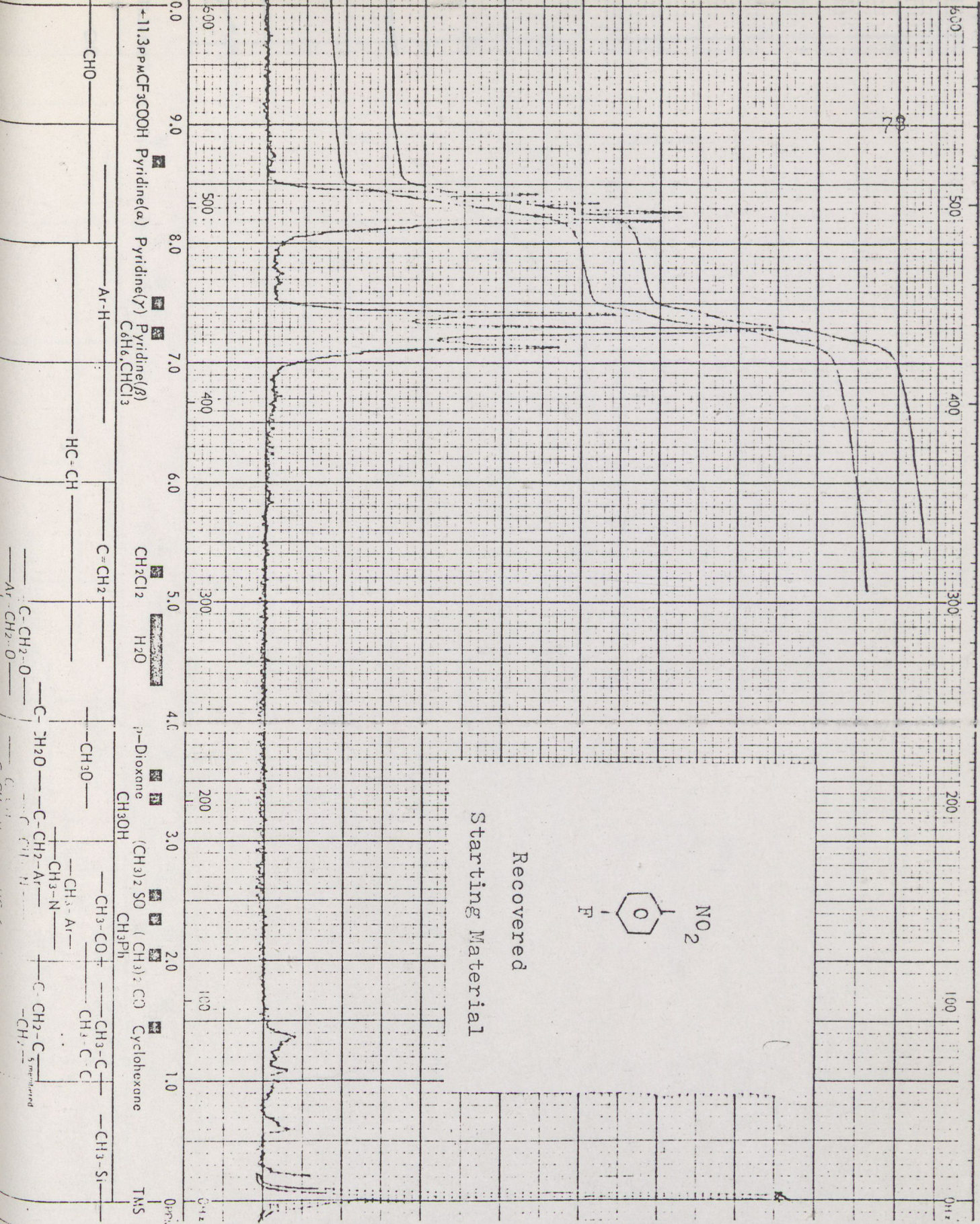
REMARKS:

15

Neu. 1



Recovered  
Starting Material





<sup>1</sup>H SPECTRUM NO: 76

SAMPLE:

REFERENCE: TMS  
SOLVENT: DMSO-d<sub>6</sub>  
CONC: Dilute

AMPLITUDE: 9  
SPECTRUM INTEGRAL: 12.4 H

H<sub>1</sub> LEVEL:

H<sub>2</sub> LEVEL:

GAIN:

SWEEP WIDTH:

NOISE SCALE EXP. 3043 1650 Hz 1.000

SHIFT

SWEEP TIME

☐ 300 150 SEC ☐

DATE: 5/6/75

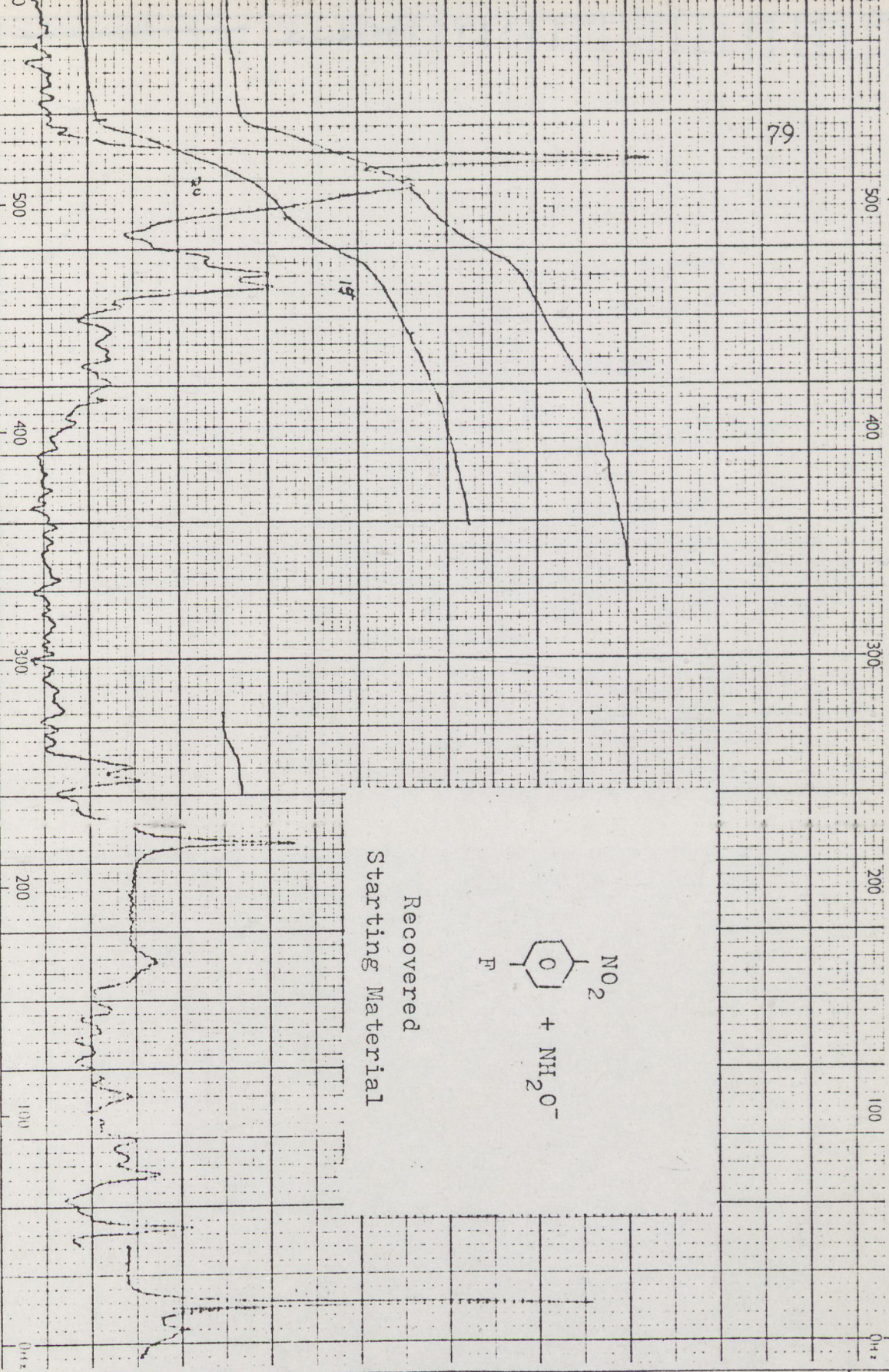
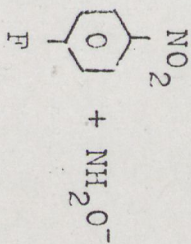
OPERATOR: H. Kemmelt

REMARKS:

Basic layer

10% excess base

1440417



1.3 ppm CF<sub>3</sub>COOH Pyridine(α) Pyridine(γ) C<sub>6</sub>H<sub>6</sub>, CHCl<sub>3</sub>

Pyridine(β)

CH<sub>2</sub>Cl<sub>2</sub> H<sub>2</sub>O

p-Dioxane CH<sub>2</sub>OH

(CH<sub>3</sub>)<sub>2</sub>SO (CH<sub>3</sub>)<sub>2</sub>CO Cyclohexane CH<sub>3</sub>Ph

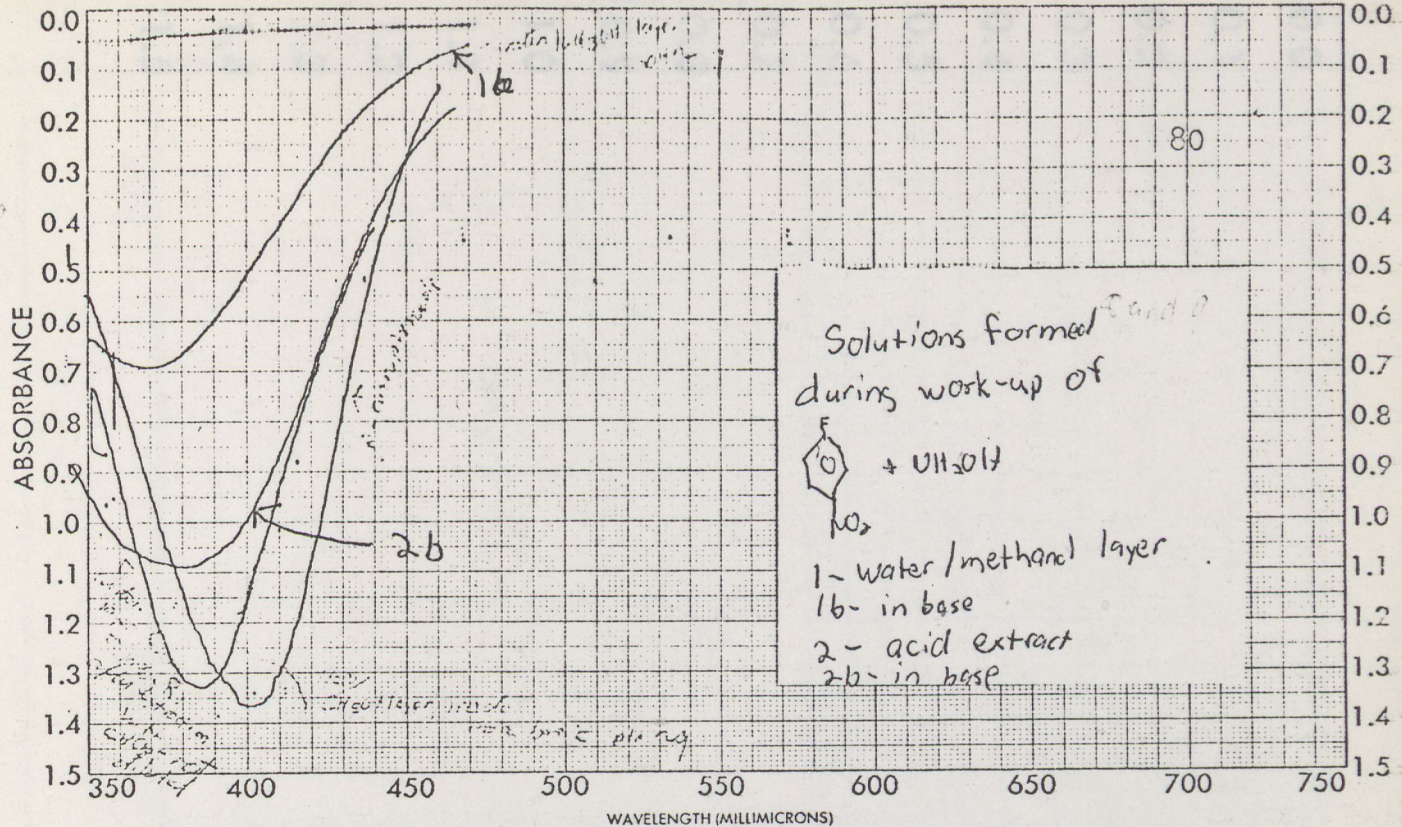
CH<sub>3</sub>-CO- CH<sub>3</sub>-C- CH<sub>3</sub>-Si-

CH<sub>3</sub>-N- CH<sub>3</sub>-C- CH<sub>2</sub>-C- CH<sub>2</sub>-C-

Ar-CH<sub>2</sub>-O- C-CH<sub>2</sub>-O- C-CH<sub>2</sub>-O- C-CH<sub>2</sub>-O-

HC=CH- Ar-H- CHO-



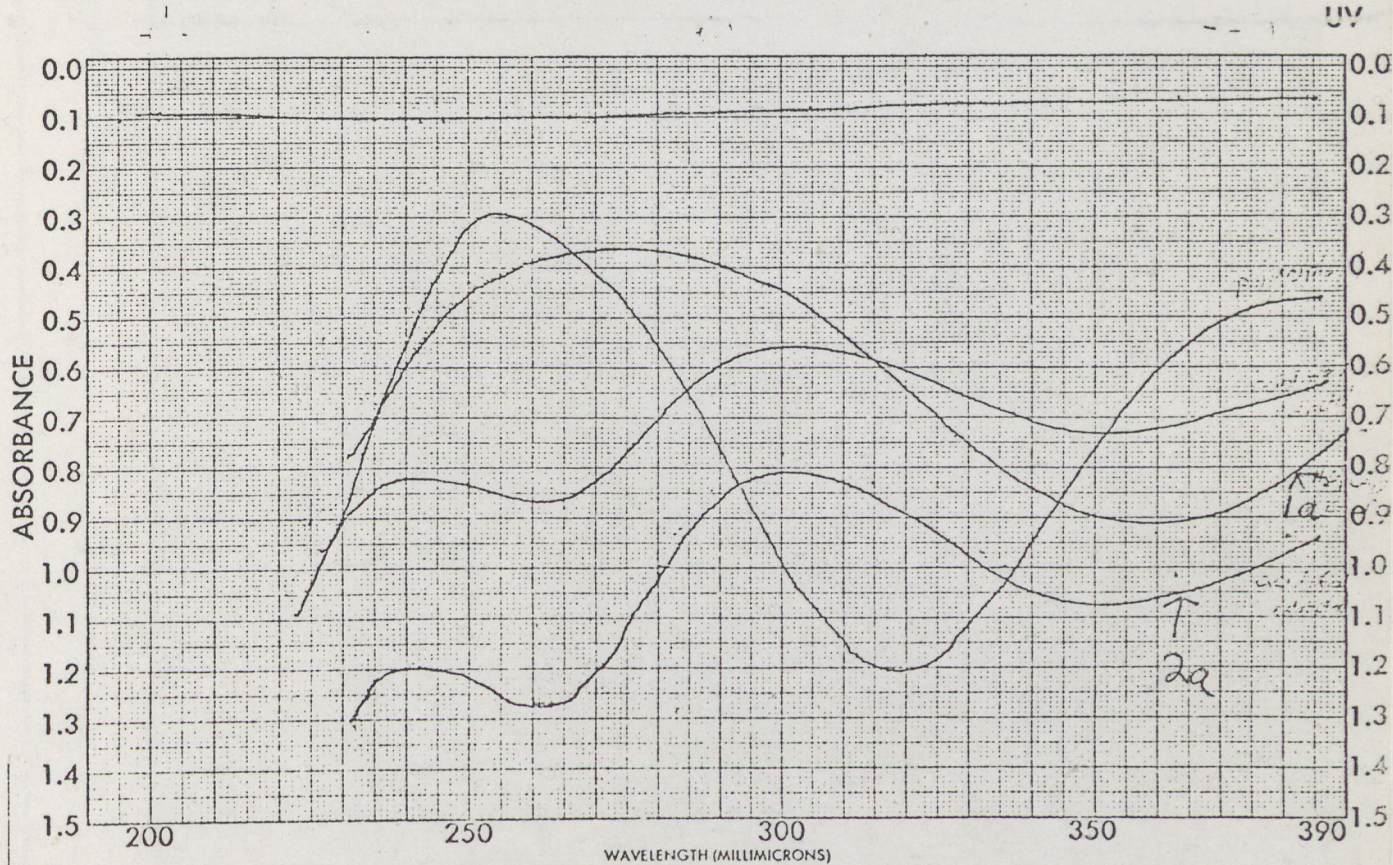


SAMPLE <i>2-nitrophenol in water</i>	CURVE NO. _____	SCAN SPEED <i>Fast</i>	OPERATOR <i>H. Kemmer</i>
ORIGIN _____	CONC. _____	SLIT <i>300</i>	DATE <i>5-1-75</i>
SOLVENT _____	CELL PATH _____	REMARKS <i># Kemmer</i>	
REFERENCE _____			

PR 11 (202-1512)

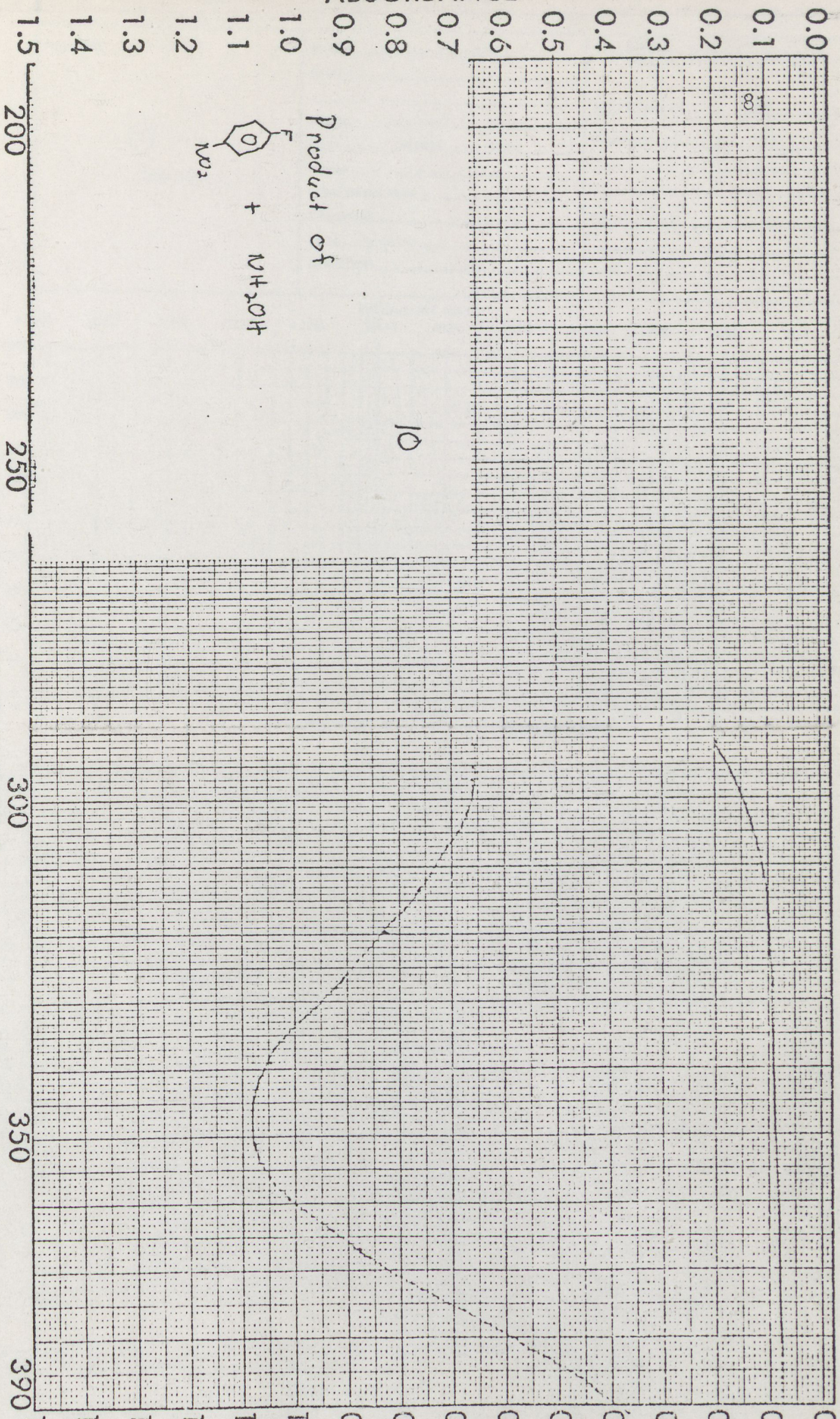
PRINTED IN U.S.A.

RECORDING CHARTS GRAPHIC CONTROLS CORPORATION BUFFALO, NEW YORK



SAMPLE <i>2-nitrophenol in H2O</i>	CURVE NO. _____	SCAN SPEED <i>Fast</i>	OPERATOR <i>5/1/75</i>
<i>Acid extract layer, CH2Cl2/H2O layer</i>	CONC. _____	SLIT <i>650</i>	DATE <i>H. Kemmer</i>
ORIGIN _____	CELL PATH _____	REMARKS _____	
SOLVENT <i>Water</i>	REFERENCE _____		





SAMPLE <i>Product</i>		CURVE NO. _____	SCAN SPEED <i>Fast</i>	OPERATOR <i>H. Williams</i>
ORIGIN <i>10% eth</i>		CONC. _____	SPLIT _____	DATE <i>5/10/95</i>
CELL PATH _____		REMARKS _____		



REMARKS

 $\text{NH}_2 \cdot \text{HCl}$ ORIGIN in Kojell

PURITY \_\_\_\_\_

SPEED \_\_\_\_\_ NORMAL \_\_\_\_\_ FAST \_\_\_\_\_

SLITS \_\_\_\_\_ NORMAL \_\_\_\_\_ WIDE \_\_\_\_\_

PHASE \_\_\_\_\_

CONCENTRATION \_\_\_\_\_

THICKNESS \_\_\_\_\_

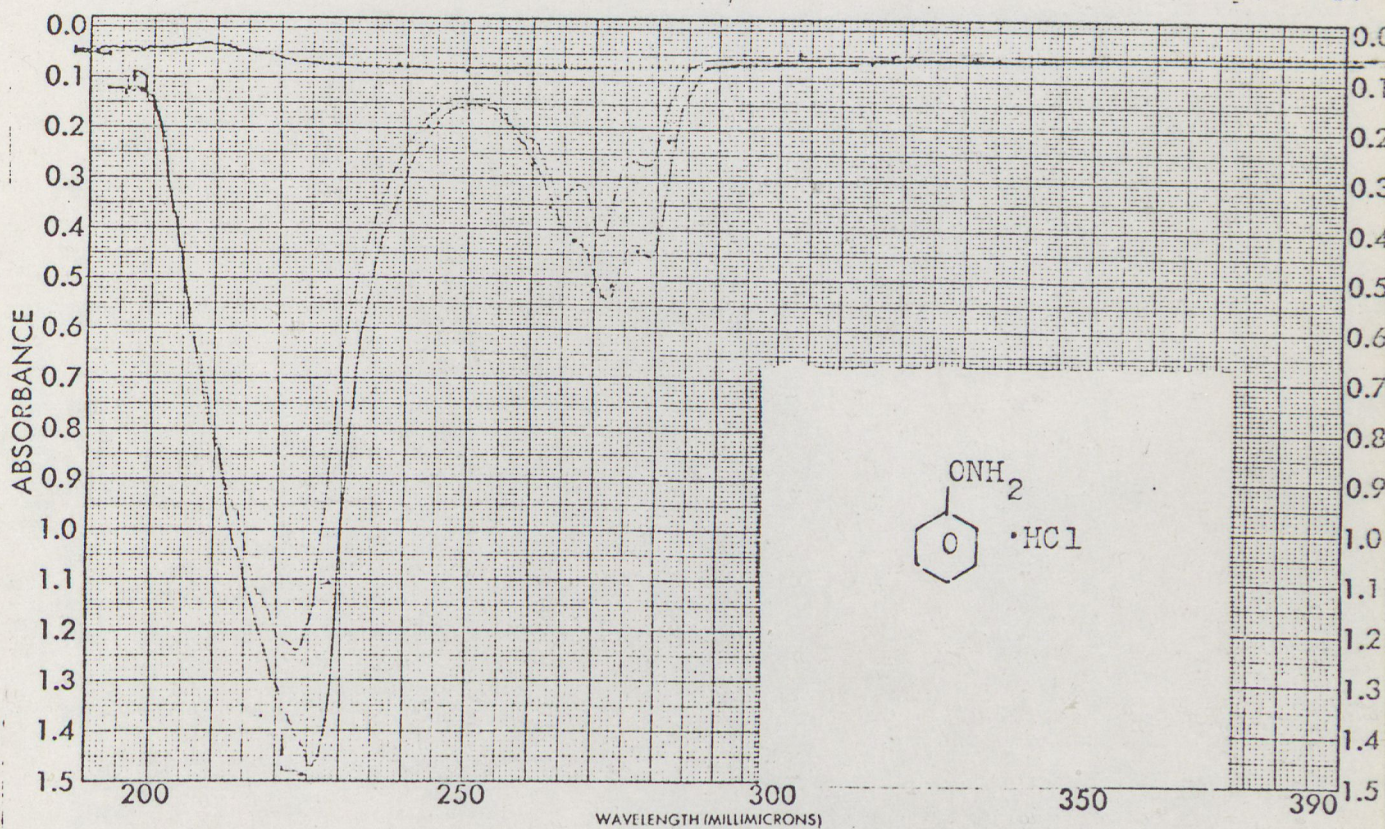
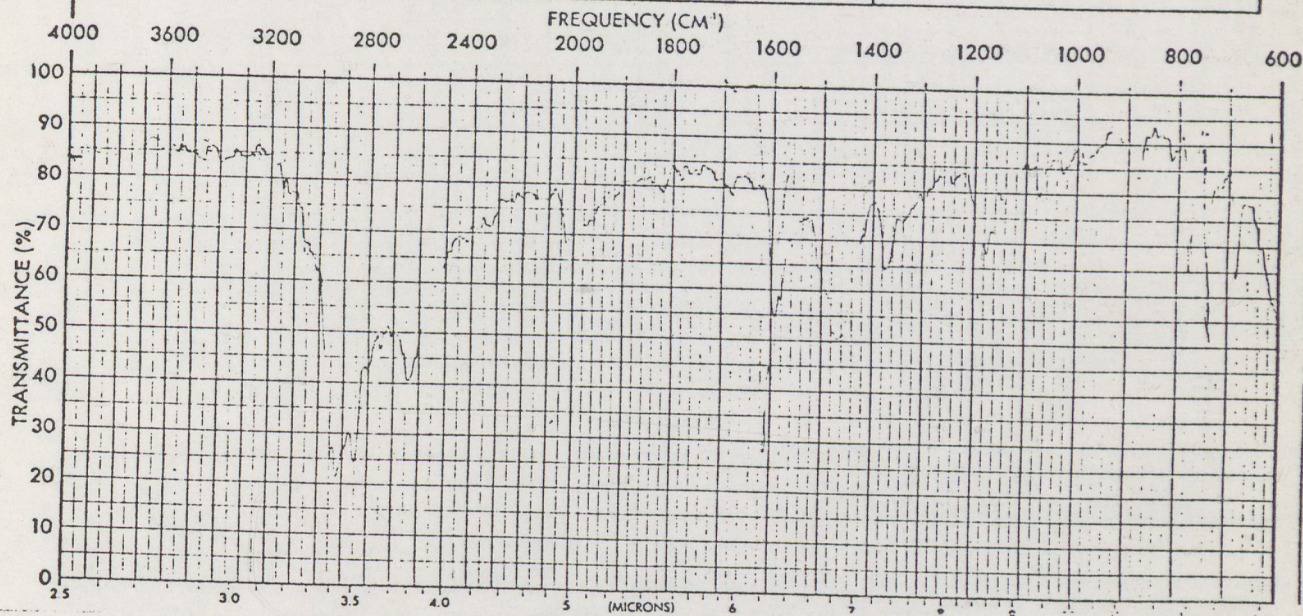
DATE 6/4/76OPERATOR H. Kennick

PERKIN-ELMER

SPECTRUM NO. 82

SAMPLE 1 \_\_\_\_\_

SAMPLE 2 \_\_\_\_\_

SAMPLE O-phenyl hydroxyamine · HCl

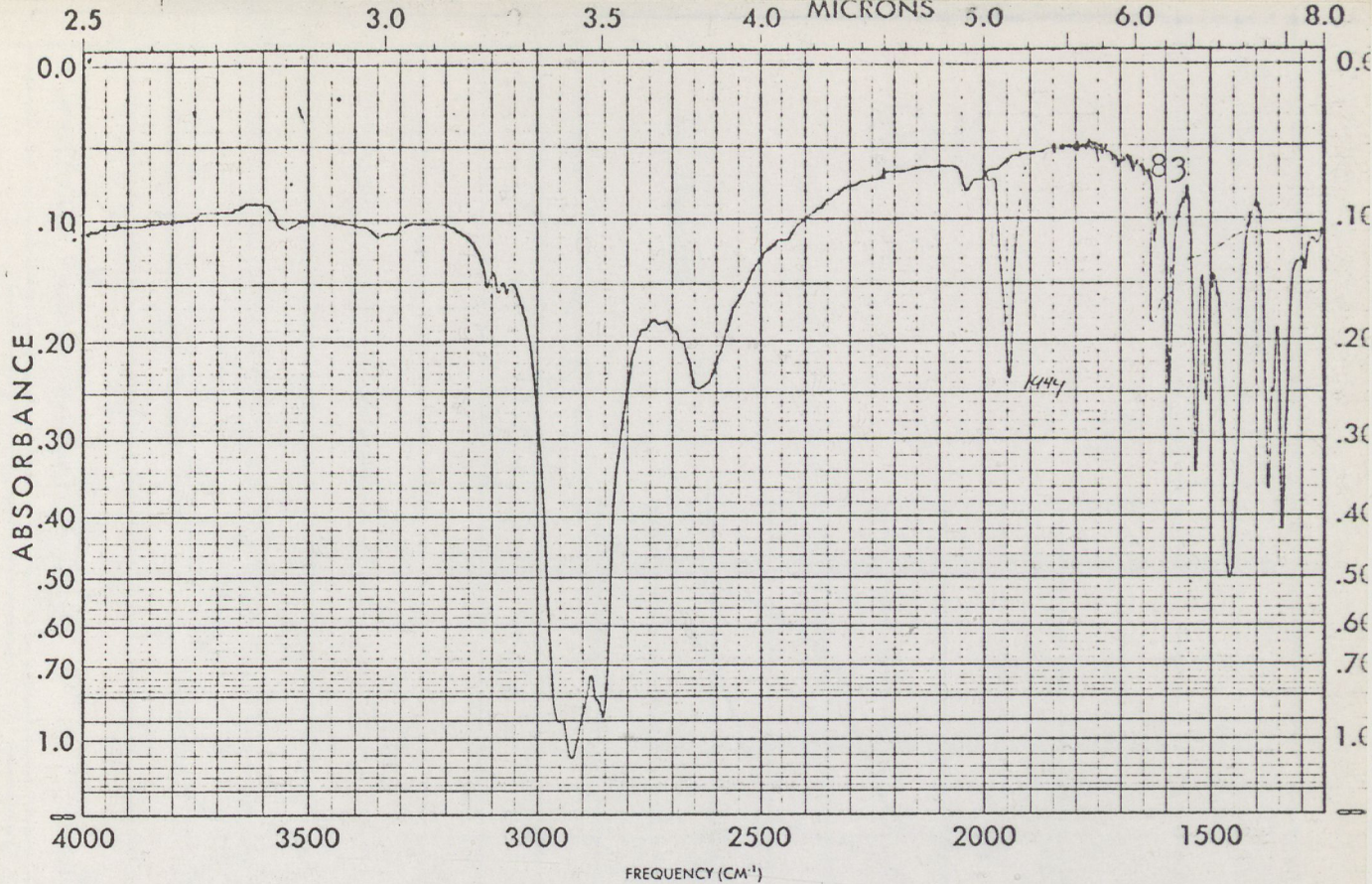
CURVE NO. \_\_\_\_\_

CONC. 3.160<sup>-4</sup> MSCAN SPEED FastOPERATOR H. KennickSLIT 70DATE 6/4/76ORIGIN hydroxyamine O-sulfonate + phenylCELL PATH 1 cmSOLVENT water

REFERENCE \_\_\_\_\_

REMARKS Lower curve has 1090excess base added - strongly basic



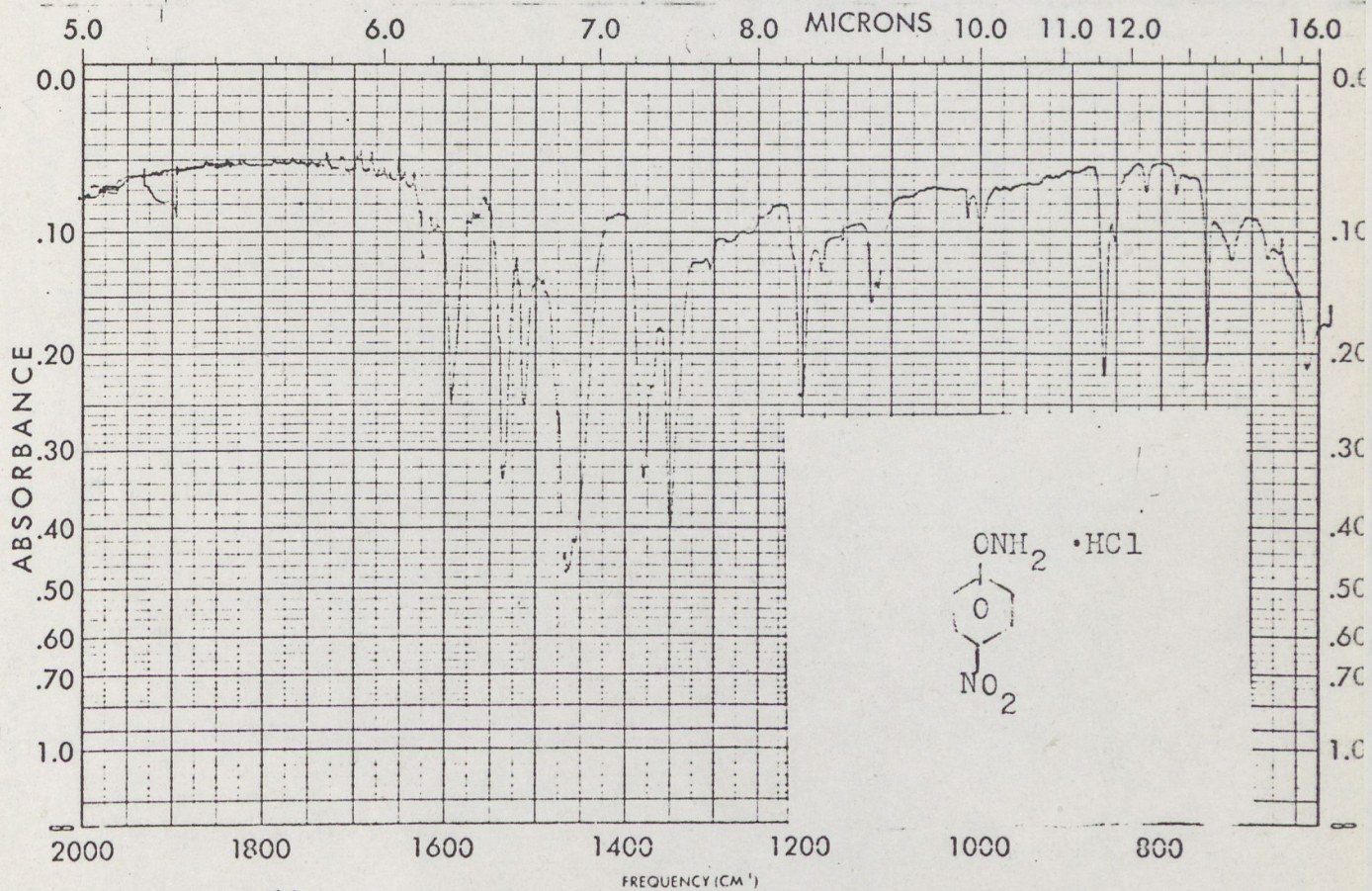


SAMPLE	<chem>NC1=CC=C(C=C1)[N+](=O)[O-]</chem> • HCl	CURVE NO.	SCAN SPEED <i>Fast</i>	OPERATOR <i>H. Kennicott</i>
ORIGIN	<chem>NO2</chem>	CONC.	SLIT <i>2025</i>	DATE <i>2/18/76</i>
SOLVENT	<i>Kuich Mull</i>	CELL PATH	REMARKS	
		REFERENCE		

NO. PR 19R (237-1032)

PRINTED IN U.S.A.

RECORDING CHARTS GRAPHIC CONTROLS CORPORATION BUFFALO, NEW YORK

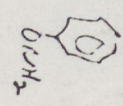


SAMPLE	<chem>NC1=CC=C(C=C1)[N+](=O)[O-]</chem> • HCl	CURVE NO.	SCAN SPEED <i>Fast</i>	OPERATOR <i>H. Kennicott</i>
ORIGIN	<chem>NO2</chem>	CONC.	SLIT <i>2025</i>	DATE <i>2/18/76</i>
SOLVENT	<i>Kuich Mull</i>	CELL PATH	REMARKS	
		REFERENCE		



1H SPECTRUM NO.:

SAMPLE:



REFERENCE: TMS  
SOLVENT: Decane  
CONC: 100%

AMPLITUDE:  
SPECTRUM:  
INTEGRAL:

H1 LEVEL:

H2 LEVEL:

GAIN:

SWEEP WIDTH:

SCALE EX

100% 600 500 400 300

SHIFT

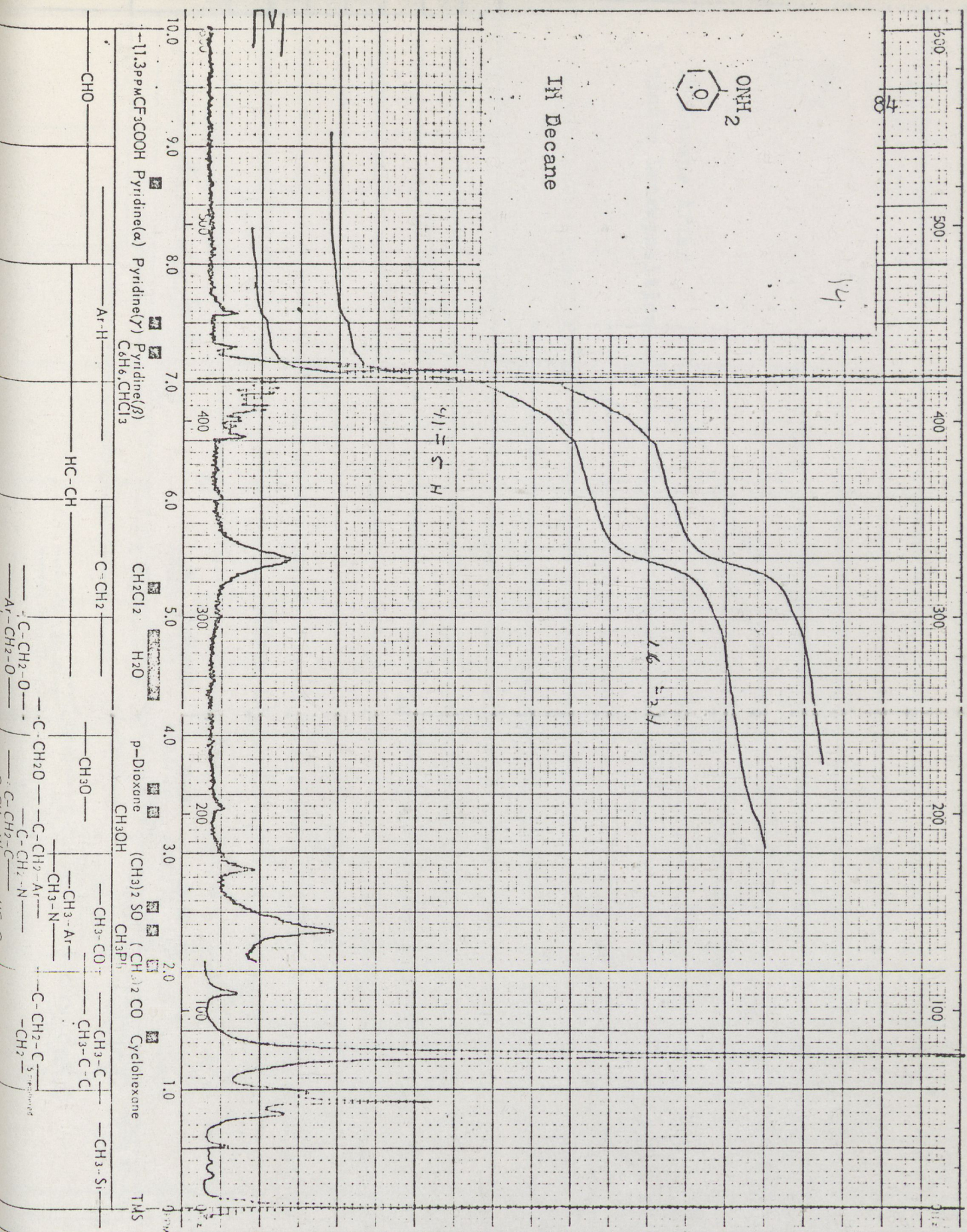
SWEEP TIME

☐ 300/150 SEC ☐

DATE:

OPERATOR

REMARKS:











16



-Ar-H

$$\text{HC} \cdot \text{CH}$$
 $\text{C}-\text{CH}_2$  $\text{CH}_2\text{Cl}_2$ H<sub>2</sub>O
$$-\text{CH}_3\text{O}-$$

p-Dioxan

 $\text{CH}_3\text{OH}$ 

(C)

CH<sub>3</sub>P

10

1

 $2\text{CO}$ 

10

cyclone

1

ne

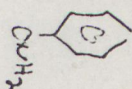
145

REMARKS:

after 5 minutes

<sup>1</sup>H SPECTRUM NO.:

SAMPLE:



REFERENCE: *Tris*  
SOLVENT: *Acetone*  
CONC: *10 g/l*

SOLVENT:...

CONC:.....

AMPLITUDE:

SPECTRUM

INTEGRAL

H1 LEVEL:

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	87	88	89	90	91	92	93	94	95	96	97	98	99	100
---	---	---	---	---	---	---	---	---	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	-----

H2 LEVEL:

**GAIN:**

SWEEP WIDTH:

NOR SCALE EX

[illegible]

SHIFT

50H1600H1

SWEEP TIME

☐ 300/150 SEC ☐

DATE:

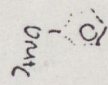
OPERATOR

REMARKS:



1H SPECTRUM NO.:

SAMPLE: .....



REFERENCE: 7728  
SOLVENT: Decane  
CONC: 1.0  
AMPLITUDE: 11  
SPECTRUM INTEGRAL

H1 LEVEL:

HI NR

H2 LEVEL:

GAIN:

XI 1/2

SWEEP WIDTH:

NOR SCALE EXP.

10PPM/600 500 400 300 2

SHIFT

SOFT SCORPE

SWEEP TIME

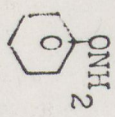
300/150 SEC

DATE:

OPERATOR

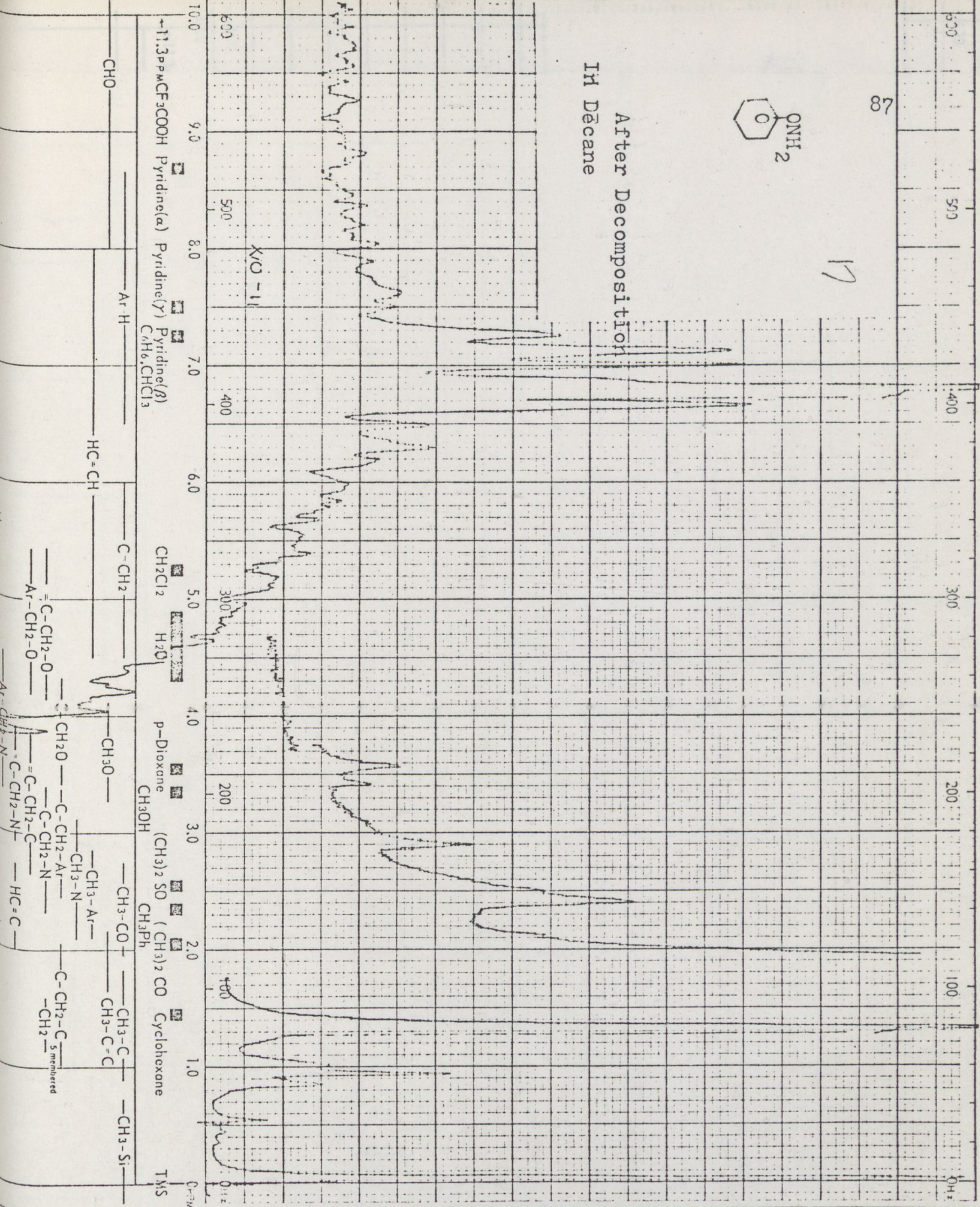
REMARKS:

After decomps.



87

After Decomposition  
In Decane



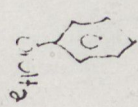












Chlor. 9 minutes



1H SPECTRUM NO.:

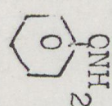
SAMPLE: .....



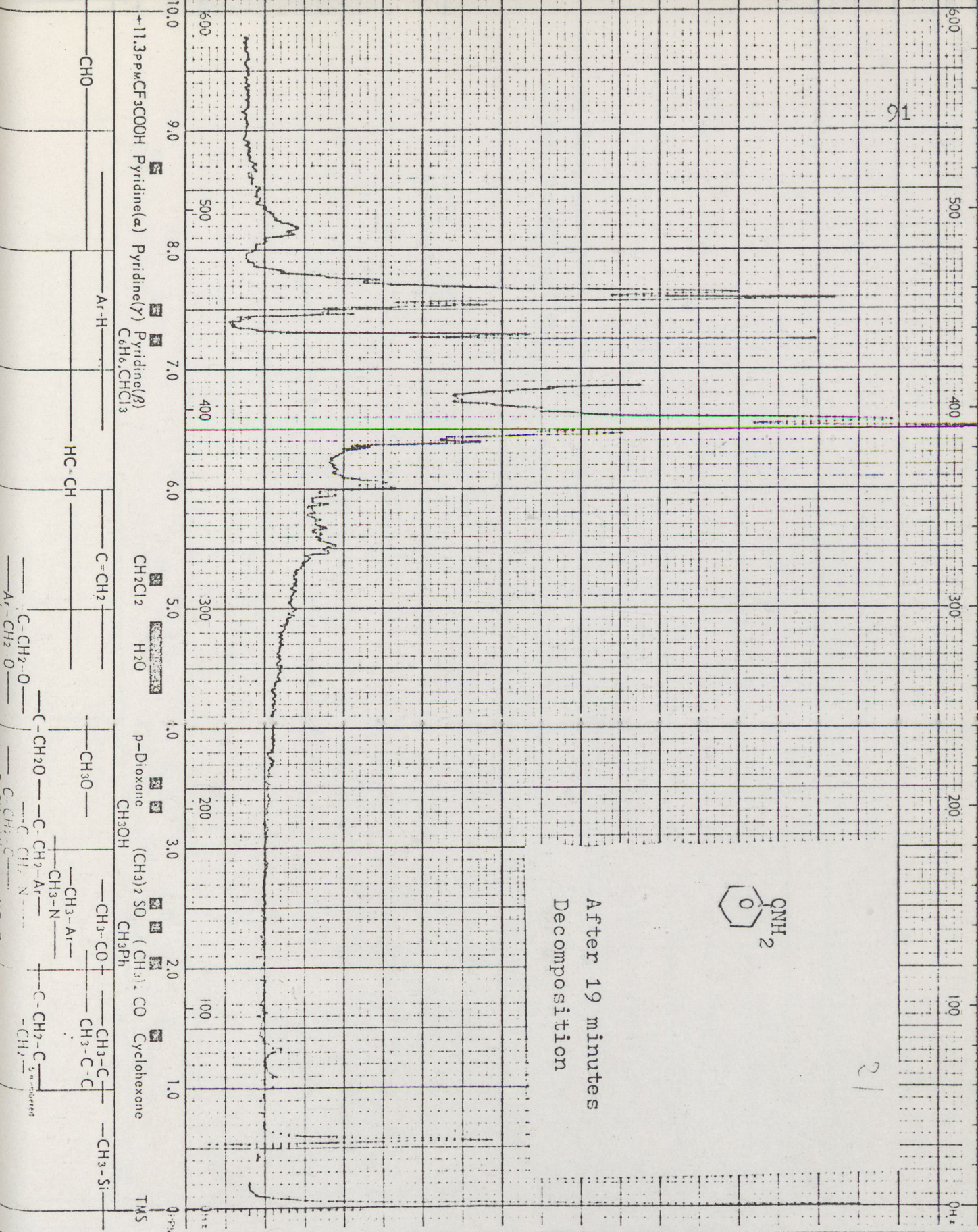
REFERENCE: *THS*  
SOLVENT: *CH<sub>2</sub>Cl<sub>2</sub>*  
CONC: .....  
AMPLITUDE: .....  
SPECTRUM: .....  
INTEGRAL: .....  
H<sub>1</sub> LEVEL: .....  
H<sub>2</sub> LEVEL: .....  
GAIN: .....  
SWEEP WIDTH: .....  
SCALE EXP: .....  
NO: .....  
SHIFT: .....  
SWEPT TIME: .....  
☐ 300/150 SEC ☐

REMARKS:

*19 minutes*

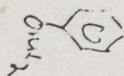


After 19 minutes  
Decomposition





SAMPLE: .....



REFERENCE: *This*  
SOLVENT: *Chloro*  
CONC: .....

AMPLITUDE: 13  
SPECTRUM  
INTEGRAL

H1 LEVEL:

H2 LEVEL: .....  
GAIN: 2

GALEIN.

SWEET WIDTH: 2 X 10

NOR SCALE EXP.

1000 500 400 300 200

SHIFT

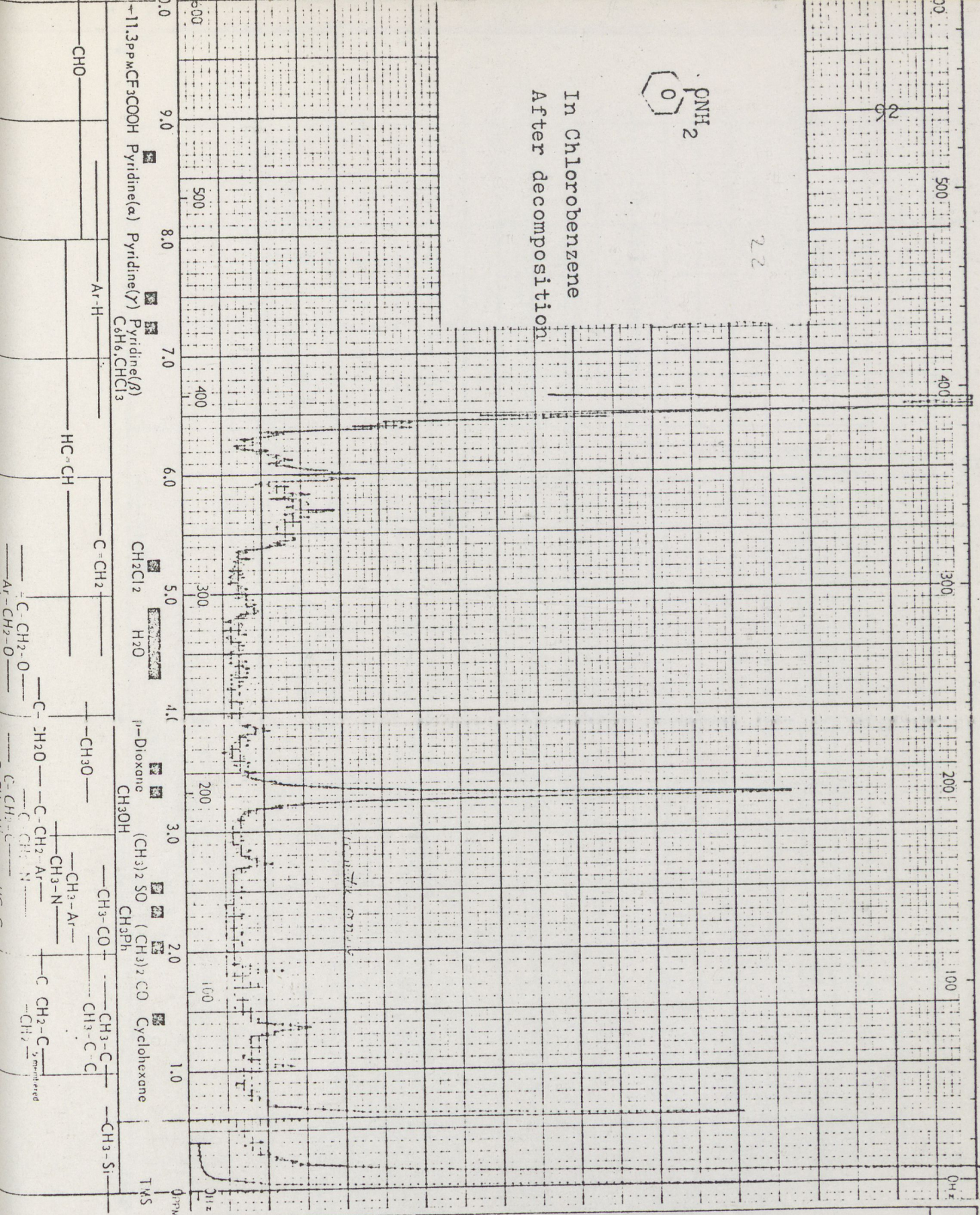
← ←

SWEEP TIME  
☐ 300/150 SEC ☐

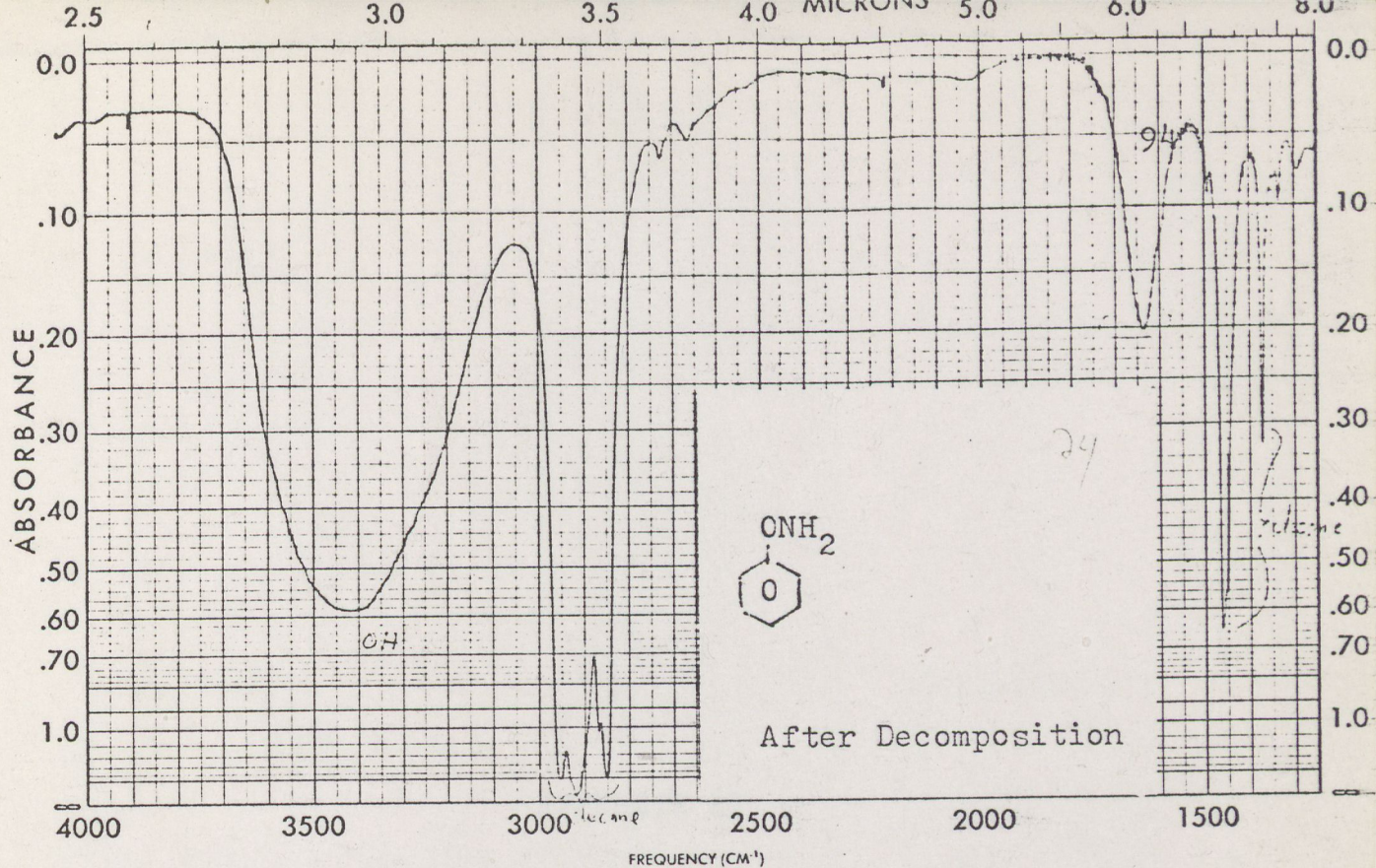
DATE:

OPERATOR

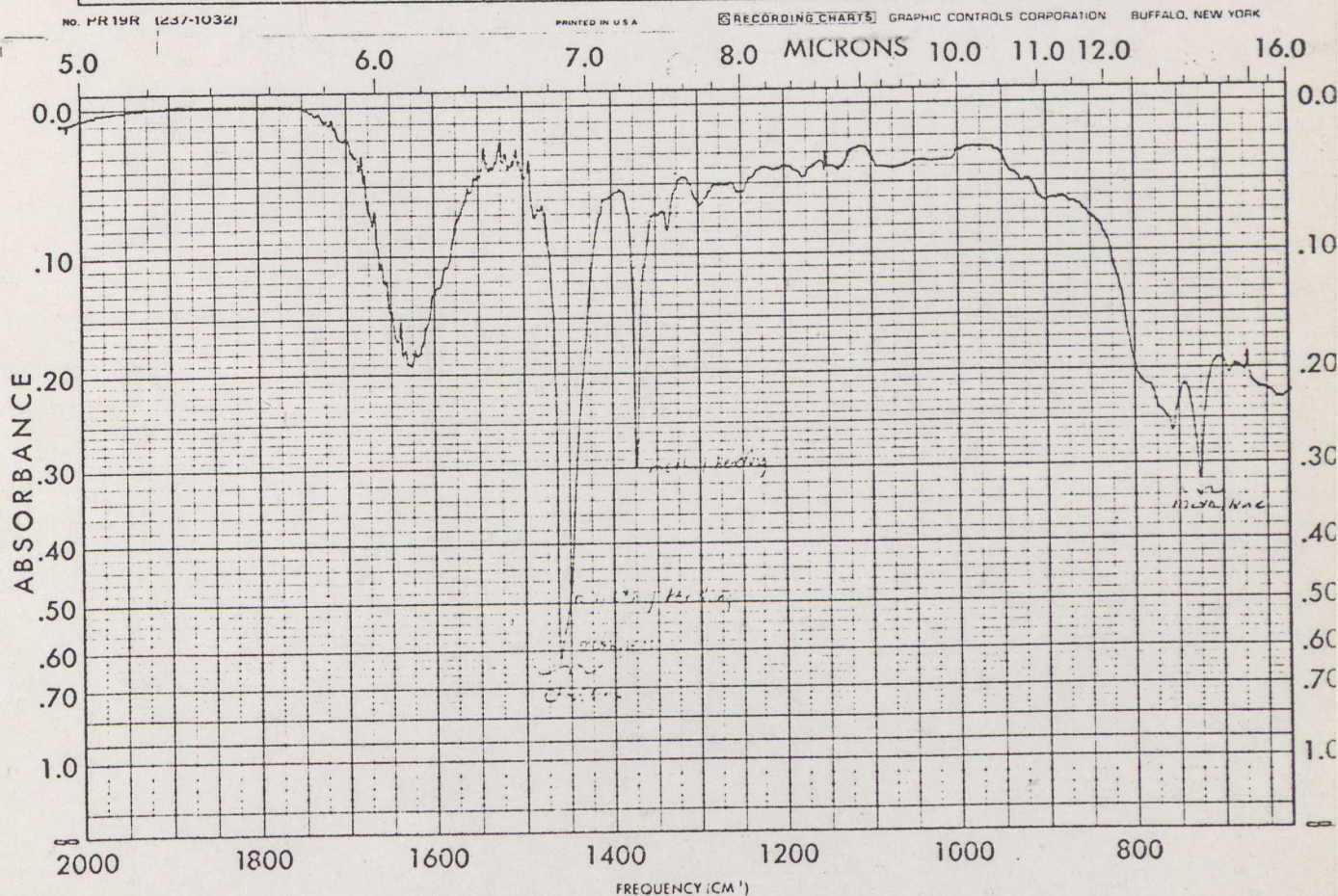
REMARKS: after dinner







SAMPLE <chem>Nc1ccccc1</chem> after decomposition	CURVE NO. _____	SCAN SPEED _____	OPERATOR H. Kern. cat
ORIGIN _____	CONC. 10%	SLIT _____	DATE 2/25/76
SOLVENT Decane	CELL PATH 10mm	REMARKS _____	
REFERENCE _____			



SAMPLE <chem>Nc1ccccc1</chem> after decomposition	CURVE NO. _____	SCAN SPEED _____	OPERATOR H. Kern. cat
ORIGIN _____	CONC. 10%	SLIT _____	DATE 2/25/76
SOLVENT Decane	CELL PATH 10mm	REMARKS _____	
REFERENCE _____			



APPENDIX II



Table 10

Heats of Reaction

<u>Reaction 8</u>	<u>H in Kcal</u>
$\text{NH}_2\text{OH} \longrightarrow {}^+\text{NH}_2 + {}^-\text{OH}$	64
$\text{NH}(\text{CH}_3)\text{OH} \longrightarrow {}^+\text{NH}(\text{CH}_3) + {}^-\text{OH}$	62
$\text{N}(\text{CH}_3)_2\text{OH} \longrightarrow {}^+\text{N}(\text{CH}_3)_2 + {}^-\text{OH}$	53
$\text{NH}_2\text{OH} \longrightarrow {}^+\text{NH}_2 + {}^-\text{OH}$	300
$\text{NH}(\text{CH}_3)\text{OH} \longrightarrow {}^+\text{NH}(\text{CH}_3) + {}^-\text{OH}$	254
$\text{N}(\text{CH}_3)_2\text{OH} \longrightarrow {}^+\text{N}(\text{CH}_3)_2 + {}^-\text{OH}$	237



1 0 1  
RADICAL

97  
OPTIMIZE GEOMETRY FOR RADICAL SPECIES  
OH RADICAL OPTIMIZE GEOMETRY

075322

HEAT OF FORMATION 16.86703 KCAL/MOLE

MULTIPLICITY 0 2

ONE ELECTRON IN ORBITAL 4

HALF ELECTRON CORRECTION -0.25 (11/11) = .1452000E-02

IONIZATION POTENTIAL 8.0880 EV

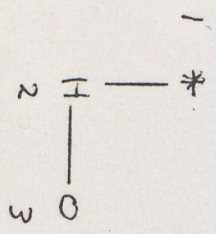
TOTAL ENERGY -389.7034 + 66.0170 = -323.6864 EV

DIPOLE MOMENT 1.6465 DEBYE

ATOM NUMBER (1)	ATOMIC NUMBER 99	BOND LENGTH (ANGSTROMS) JO1	BOND ANGLE (DEGREES) KOJO1	TWIST ANGLE (DEGREES) LOKOJO1	J	K	L	ATOM NUMBER I	X	Y	Z	COORDINATES
1	99	1.0000						1	-1.00000	0.00000	0.00000	0.00000
2	1	0.9476 *	0.000		1			2	0.00000	0.00000	0.00000	0.00000
3	8				2	1		3	0.94759	0.00000	0.00000	0.00000

COMPUTATION TIME = 30.37 SECONDS

SCF CALCULATIONS = 4



\* = Dummy atom



1 0 1  
ANION

OPTIMIZE GEOMETRY FOR RADICAL SPECIES

HYDROXIDE ION OPTIMIZE GEOMETRY

80

HEAT OF FORMATION -6.70272 KCALS/MOLE

075322

CHARGE -1

IONIZATION POTENTIAL 1.2236 EV

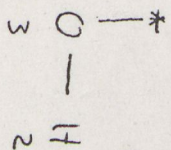
TOTAL ENERGY -390.6809 + 65.9733 = -324.7076 EV

DIPOLE MOMENT 7.3239 DEBYE

ATOM NUMBER (1)	ATOMIC NUMBER	BOND LENGTH (ANGSTROMS) JOI	BOND ANGLE (DEGREES) KJOI	TWIST ANGLE (DEGREES) LOKJOI	ATOM NUMBER	COORDINATES
1	99				1	X Y Z
2	1	1.0000			2	0.00000 0.00000 0.00000
3	8	0.9486 *	90.000		3	0.00000 0.00000 0.00000

COMPUTATION TIME = 28.62 SECONDS

SCF CALCULATIONS = 4





2 N 1  
RADICAL

66 OPTIMIZE GEOMETRY FOR RADICAL SPECIES  
NH2 RADICAL OPTIMIZE GEOMETRY

075322

HEAT OF FORMATION 30.07668 KCALS/MOLE

MULTIPLICITY 2

ONE ELECTRON IN ORBITAL 4

HALF ELECTRON CORRECTION -0.25 (11/11) = .1296000E 02

IONIZATION POTENTIAL 5.0414 EV

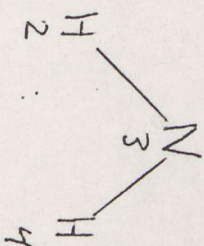
TOTAL ENERGY -331.0343 + 110.3998 = -220.6344 EV

DIPOLE MOMENTO 1.4565 DEBYE

ATOM NUMBER (1)	ATOMIC NUMBER	BOND LENGTH (ANGSTROMS) JO1	BOND ANGLE (DEGREES) KOJO1	TWIST ANGLE (DEGREES) LOKOJO1	J	K	L	ATOM NUMBER I	X	COORDINATES Y	Z
1	99	1.0000						1	0.00000	0.00000	0.00000
2	1	1.0360 *	90.000		1			2	1.00000	0.00000	0.00000
3	7	1.0360	102.194 *	0.000	2	1		3	1.00000	1.03598	0.00000
4	1	1.0360			3	2	1	4	-0.01260	1.25481	0.00000

COMPUTATION TIME 151.58 SECONDS

SCF CALCULATIONS 10





2 N 1  
CATION

ONH2 POSITIVE ION OPTIMIZE

FIRST RUN SP2 BEOMETRY INPUT

075281

HEAT OF FORMATION 289.83602 KCALS/MOLE

CHARGE 1

IONIZATION POTENTIAL 21.5727 EV

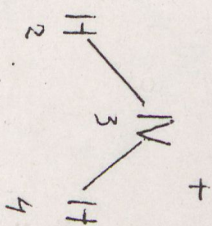
TOTAL ENERGY -319.4273 + 110.0568 = -209.3704 EV

DIPOLE MOMENTO 4.7839 DEBYE

ATOM NUMBER (1)	ATOMIC NUMBER	BOND LENGTH (ANGSTROMS) JOI	BOND ANGLE (DEGREES) KJOI	TWIST ANGLE (DEGREES) LOKJOI	J	K	L	ATOM NUMBER I	X	Y	Z
1	99	1.0000			1			1	0.00000	0.00000	0.00000
2	1	1.0386 *	90.000		2	1		2	1.00000	0.00000	0.00000
3	7	1.0386	106.048 *	0.000	3	2	1	3	1.00000	1.03859	0.00000
4	1	1.0386						4	0.00188	1.32570	0.00000

COMPUTATION TIME 107.23 SECONDS

SCF CALCULATIONS 10





1 H 4 N 1  
RADICAL

101 OPTIMIZE GEOMETRY FOR RADICAL SPECIES  
(NH)CH3 RADICAL OPTIMIZE GEOMETRY

075322

HEAT OF FORMATION 33.72734 KCALS/MOLE

MULTIPLICITY 0 2

ONE ELECTRON IN ORBITAL 7

HALF ELECTRON CORRECTION -0.25 (II/II) = .10575244E 02.

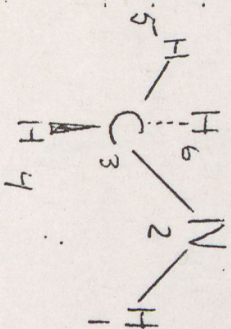
IONIZATION POTENTIAL 4.6737 EV TOTAL ENERGY -857.1654 -480.3003 -376.8651 EV

DIPOLE MOMENTO 1.3518 DEBYE

ATOM NUMBER (I)	ATOMIC NUMBER	BOND LENGTH (ANGSTROMS) JOI	BOND ANGLE (DEGREES) KJOI	TWIST ANGLE (DEGREES) LOKJOI	J	K	L	ATOM NUMBER I	X	Y	Z
1	1	1.0291 *			1			1	0.00000	0.00000	0.00000
2	7	1.02913	113.582 *		2			2	1.02913	0.00000	0.00000
3	6	1.3588 *	115.326 *	90.571 *	3	1	1	3	1.57272	1.24532	0.00000
4	1	1.1173			4			4	1.77316	1.67932	-1.00989
5	1	1.1173	115.326	331.551 *	5	2	1	5	0.95010	2.03860	0.48111
6	1	1.1173	115.326	208.802 *	6	2	1	6	2.57502	1.32931	0.48658

COMPUTATION TIME 736.35 SECONDS

SCF CALCULATIONS 16





1 H 4 N 1  
CATION

02 (NH)CH3 POSITIVE ION OPTIMIZE  
101 FIRST RUN SP2 GEOMETRY INPUT

075281

HEAT OF FORMATION 248.93272 KCALS/MOLE

CHARGED 1

IONIZATION POTENTIAL 17.6375 EV

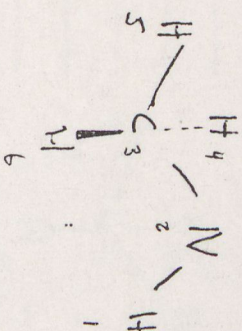
TOTAL ENERGY -851.3108 + 483.7576 = -367.5531 EV

DIPOLE MOMENT 7.2594 DEBYE

ATOM NUMBER (I)	ATOMIC NUMBER	BOND LENGTH (ANGSTROMS)	BOND ANGLE (DEGREES)	TWIST ANGLE (DEGREES)	ATOM NUMBER	COORDINATES
1	1				1	X Y Z
2	7	1.0326 *			2	0.00000 0.00000 0.00000
3	6	1.5266 *	118.944 *		3	0.00000 0.00000 0.00000
4	1	1.1235 *	112.380 *	90.930 *	4	1.16046 1.52649 -1.03875
5	1	1.1235	112.380	335.486 *	5	1.89752 1.05592 0.43105
6	1	1.1235	112.380	205.996 *	6	2.69959 1.08218 0.45536

COMPUTATION TIME = 606.30 SECONDS

SCF CALCULATIONS = 11





2 H 6 N 1  
RADICAL

103 OPTIMIZE GEOMETRY FOR RADICAL SPECIES  
N(CH3)2 RADICAL OPTIMIZE GEOMETRY

075322

HEAT OF FORMATION 43.81467 KCAL/MOLE

MULTIPLICITY 0 2

ONE ELECTRON IN ORBITAL 10

HALF ELECTRON CORRECTION -0.25 ( (11/11) = .10517840E 02 )

IONIZATION POTENTIAL 4.3356 EV

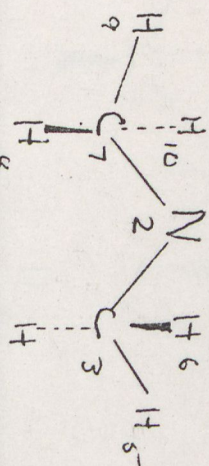
TOTAL ENERGY -1516.5570 + 985.7003 = -532.8567 EV

DIPOLE MOMENT 1.2482 DEBYE

ATOM NUMBER (1)	ATOMIC NUMBER	BOND LENGTH (ANGSTROMS) JOI	BOND ANGLE (DEGREES) KOUOI	TWIST ANGLE (DEGREES) LOKOUOI	J	K	L	ATOM NUMBER I	X	Y	Z
1	99	1.0000						1	0.00000	0.00000	0.00000
2	7	1.4700 *	120.000		1			2	1.00000	0.00000	0.00000
3	6	1.0950 *	109.400	90.000	2	1		3	1.73500	1.27306	0.00000
4	1	1.0950	109.400	330.000	3	2	1	4	1.91686	1.58805	0.00000
5	1	1.0950	109.400	210.000	3	2	1	5	1.14224	2.03527	0.51641
6	1	1.0950	120.000 *	90.000 *	2	3	4	6	2.69148	1.14082	0.51641
7	6	1.4700	109.400	90.000	2	3	1	7	-0.47000	0.00000	-0.00000
8	1	1.0950	109.400	330.000	7	2	1	8	-0.83372	-0.75483	-0.70496
9	1	1.0950	109.400	210.000	7	2	1	9	-0.83372	-0.23310	1.00618
10	1	1.0950	109.400		7	2	1	10	-0.83372	0.98793	-0.30122

COMPUTATION TIME = 1092.32 SECONDS

SCF CALCULATIONS = 12





2 H 6 N 1  
CATION

104

N(CH3)2 POSITIVE ION OPTIMIZE  
FIRST RUN (NH)CH3 GEOMETRY I PUT

075299

HEAT OF FORMATION 235.90489 KJALS/MOLE

CHARGE 1

IONIZATION POTENTIAL 16.3594 EV

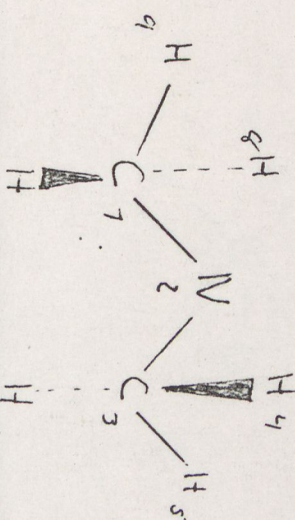
TOTAL ENERGY -1531.7447 + 1007.2177 = -524.5270 EV

DIPOLE MOMENTO 4.0469 DEBYE

ATOM NUMBER (1)	ATOMIC NUMBER	BOND LENGTH (ANGSTROMS) JOI	BOND ANGLE (DEGREES) KJOI	TWIST ANGLE (DEGREES) LOKJOI	J	K	L	ATOM NUMBER I	X	Y	Z
1	99	1.0000			1			1	0.00000	0.00000	0.00000
2	7	1.3736 *	120.000		2	1		2	1.00000	0.00000	0.00000
3	6	1.1199 *	112.036 *	90.000	3	2	1	3	1.68682	1.18961	0.00000
4	1	1.1199	112.036	350.000	4	2	1	4	1.69692	1.55350	-1.03813
5	1	1.1199	112.036	210.000	5	2	1	5	1.11832	2.00303	0.51906
6	1	1.1199	112.036	210.000	6	2	1	6	2.67551	1.10398	0.51906
7	6	1.3736	120.118 *	92.973 *	7	3	4	7	-0.37226	-0.00363	0.06162
8	1	1.1199	112.036	90.000	8	2	1	8	-0.79202	1.03158	0.14156
9	1	1.1199	112.036	330.000	9	2	1	9	-0.63242	-0.47006	-0.64665
10	1	1.1199	112.036	210.000	10	2	1	10	-0.75162	-0.57576	0.94650

COMPUTATION TIME = 1389.12 SECONDS

SCF CALCULATIONS = 10





H 3 N 1 0 1

NH2OH OPTIMIZE GEOMETRY

FIRST RUN SP2 AND SP3 GEOMETRY INPUT

05

075308

HEAT OF FORMATION = -16.83472 KCALS/MOLE

IONIZATION POTENTIAL = 10.0586 EV

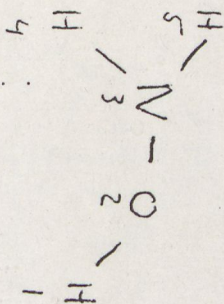
TOTAL ENERGY = -1096.0041 + 548.9184 = -547.0857 EV

DIPOLE MOMENT = 2.6974 DEBYE

ATOM NUMBER (1)	ATOMIC NUMBER	BOND LENGTH (ANGSTROMS)	BOND ANGLE (DEGREES)	TWIST ANGLE (DEGREES)	J	K	L	ATOM NUMBER I	X	COORDINATES Y	Z
1	1	0.9605 *						1	0.00000	0.00000	0.00000
2	8				1			2	0.96053	0.00000	0.00000
3	7	1.3493 *	117.084 *		2	1		3	1.57487	1.20136	0.00000
4	1	1.0547 *	111.041 *	54.621 *	3	2	1	4	1.23984	1.79801	-0.80261
5	1	1.0547	111.041	305.382 *	3	2	1	5	1.23980	1.79803	0.80258

COMPUTATION TIME = 1357.40 SECONDS

SCF CALCULATIONS = 22





1 H 5 N 1 O 1

# OPTIMIZE GEOMETRY FOR RADICAL SPECIES

106 NH CH3 OH OPTIMIZE GEOMETRY

075322

HEAT OF FORMATIONO -11.79351 KCALS/MOLE

IONIZATION POTENTIALO 9.2913 EV

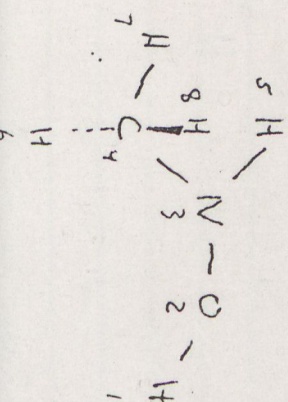
TOTAL ENERGYO -1617.7559 + 1114.4799 = -703.2760 EV

DIPOLE MOMENTO 2.5406 DEBYE

ATOM NUMBER (1)	ATOMIC NUMBER	BOND LENGTH (ANGSTROMS) JOI	BOND ANGLE (DEGREES) KOJOI	WIST ANGLE (DEGREES) LOKOJOI	J	K	L	ATOM NUMBER I	X	Y	Z
1	1	0.9627 *	116.735 *		1			1	0.00000	0.00000	0.00000
2	6	1.3521 *	117.033 *	301.306 *	2	1		2	0.96267	0.00000	0.00000
3	7	1.4283 *	113.811 *	58.036 *	3	2		3	1.57093	1.20756	0.00000
4	6	1.1193 *	113.811 *	297.102 *	4	3	1	4	1.27256	0.00000	0.00000
5	1	1.1193	113.811	177.831 *	5	4	2	5	0.18369	2.08469	1.08698
6	1	1.1193	113.811	61.342 *	6	5	2	6	1.58842	1.69027	2.08570
7	1	1.0568 *	109.864 *		7	6	1	7	1.77446	3.08242	1.01338
8	1				8	7		8	1.30674	1.74272	-0.87219

COMPUTATION TIME = 2135.43 SECONDS

SCF CALCULATIONS = 24





2 H 7 N 1 O 1

OPTIMIZE GEOMETRY

N(CH3)2NH SP2 AND SP3 GEOMETRY INPUT

075341

107

HEAT OF FORMATION = -0.75971 KCAL/MOLE

IONIZATION POTENTIAL 8.7100 EV

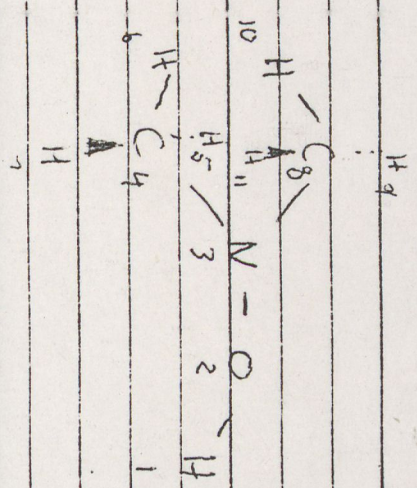
TOTAL ENERGY = -2695.4415 + 1836.2350 = -859.2065 EV

DIPOLE MOMENT 2.2847 DEBYE

ATOM NUMBER (1)	ATOMIC NUMBER	BOND LENGTH (ANGSTROMS) JOI	BOND ANGLE (DEGREES) KJOI	TWIST ANGLE (DEGREES) LKOJOI	J	K	L	ATOM NUMBER I	X	Y	Z
1	1	0.9641 *	115.617 *		1			1	0.00000	0.00000	0.00000
2	8	1.3634 *	113.327 *	295.414 *	2	1	1	2	0.96412	0.00000	0.00000
3	7	1.4292 *	113.979 *	52.962 *	3	2	2	3	1.55360	1.22939	0.00000
4	6	1.1204 *	113.979 *	292.424 *	4	3	2	4	1.29043	1.98322	1.18539
5	1	1.1204	113.979	172.838 *	5	3	2	5	0.20174	2.07723	1.43290
6	1	1.1204	113.979	74.259 *	6	3	2	6	1.76243	1.55918	2.10884
7	1	1.4292	113.327	52.962	7	2	1	7	1.66154	3.03962	1.14498
8	6	1.1204	113.979	292.424	8	3	2	8	1.47726	1.89364	-1.26318
9	1	1.1204	113.979	172.838	9	3	2	9	1.85760	1.28327	-2.12232
10	1	1.1204	113.979	74.259 *	10	3	2	10	0.43878	2.19386	-1.55773
11	1	1.1204	113.979	52.962	11	3	2	11	2.06536	2.84599	-1.31311

COMPUTATION TIME = 9317.02 SECONDS

SCF CALCULATIONS = 48





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