

104
MECHANISM OF THE OZONATION OF PYRENE
OZONIDE-ZWITTERION RELATIONSHIPS

A DISSERTATION 6/
SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR
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TABLE OF CONTENTS

ACKNOWLEDGEMENTS.....	iii
-----------------------	-----

LIST OF TABLES.....	vi
---------------------	----

Chapter

I. Introduction.....	1
II. Historical.....	3
III. Experimental	
A. Ozonation of Pyrene.....	8
1. Ozonation of Pyrene in <u>t</u> -Butyl Alcohol-Water.....	9
a. Decomposition of the Butoxyhydroxy-peroxide.....	9
b. Products of Aqueous Filtrate.....	9
2. Ozonation of Pyrene in Acetone-Water.....	10
a. Monomeric Monoozonide of Pyrene.....	10
b. Products of Aqueous Filtrate.....	10
B. Ozonation of the Monomeric Monoozonide in Acetone-Water.....	11
C. Ozonation of the Monomeric Monoozonide in Acetone-Water-Reduction with Dimethyl Sulfide.....	12
D. Ozonation of 4-Formyl-5-phenanthrene-carboxylic Acid.....	12
E. Spectroscopic Studies of the Ozonation Products.....	13
IV. Discussion	22
V. Summary	33

References

Appendix

LIST OF TABLES

Table	Page
I. Ultraviolet Absorption of Monomeric Monoozonide of Pyrene.....	15
II. Ultraviolet Absorption of 4-Formyl- 5-phenanthrenecarboxylic Acid.....	16
III. Partial Mass Spectrum of 2,2',6,6'- Biphenyltetracarboxaldehyde.....	18
IV. Partial Mass Spectrum of 2,2',6- Triformyl-6'biphenylcarboxylic Acid.....	19
V. Partial Mass Spectrum of 2,2',6,6'- Biphenyltetracarboxylic Acid.....	20
VI. Partial Mass Spectrum of 4-Formyl- 5-phenanthrenecarboxylic Acid.....	21

INTRODUCTION

Although ozone was discovered by Schonbein in 1840 (1), the first investigation of the mechanism of its formation from oxygen was that of Lind in 1911. In 1968, Sears and Sutherland (2) of the Brookhaven National Laboratory, reviewing Lind's work, point out that "it is thus one of the oldest systems in radiation chemistry".

The first studies of the reactions of ozone with organic compounds were made by Harries (3) at the beginning of the 20th century. Harries worked exclusively in anhydrous nonparticipating (aprotic) solvents such as chloroform. The products which he obtained were almost invariably unstable polymeric ozonides having unpredictable and violently explosive properties. The hazards of working with ozone and ozonation products discouraged all but a handful of scientists from engaging in the study. Progress in the field, therefore, did not keep pace with that made in other areas of science.

Interest in ozone and ozonation products was renewed about 20 years ago, stimulated in part by the discovery that the presence of ozone in the atmosphere and stratosphere of the earth plays an important and ever increasing part in the health and welfare of its people. Paradoxically, the potent oxidizing properties of ozone have created an important place for it in the field of antipollutants.

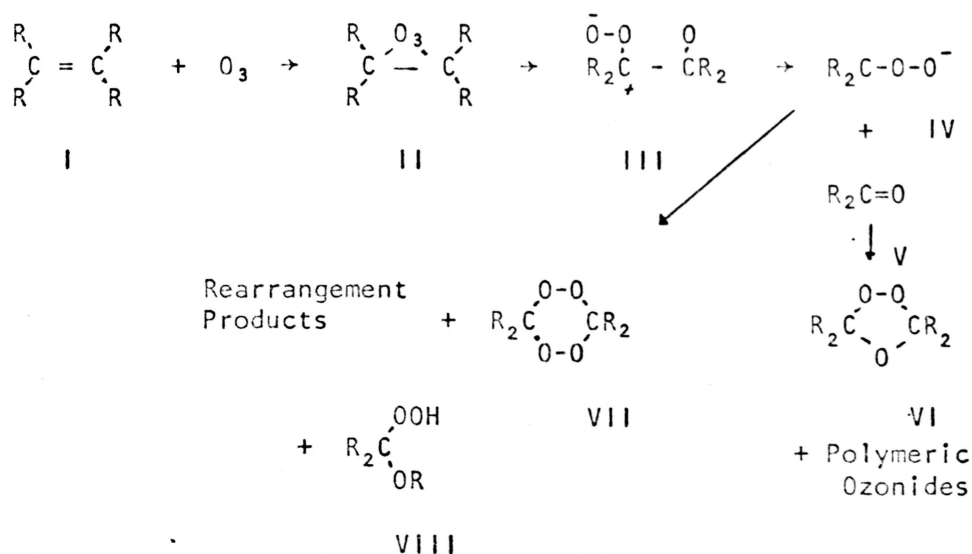
A great deal remains to be learned about ozone and its reactions. It has been the object of this investigation to make a contribution towards the complete understanding of the complex mechanism of the reactions of ozone with pyrene, a tetracyclic aromatic compound. Specifically it is directed to the ozonation of pyrene with water as a participating solvent, a novel feature introduced by Sturrock and

and co-workers (4) in 1959 in an attempt to bring about concurrent ozonation and hydrolysis of the ozonation product with the prime object of removing the explosion hazard.

HISTORICAL

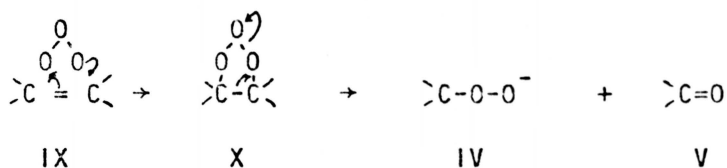
The structure of the ozone molecule has been studied by a series of investigators (5) who have determined that the ozone molecule has an obtuse angle ($116^{\circ}45' \pm 30'$) and a bond length of $1.278 \pm .002$ Å. Ozone has been produced under various conditions including the passage of oxygen through a silent electric discharge, by photolysis, by the electrolysis of water and more recently by its formation under radiolytic conditions. So far, the most practical method of making ozone is by silent electric discharge.

In 1905, Harries(3) published a report on the ozone treatment of a wide variety of compounds containing double bonds. He showed that ozone is a specific reagent for double bonds. He was not, however, concerned with the mechanism involved. In 1925, Staudinger proposed that ozone reacts with a double bond to form an initial unstable "mol-ozonide", which then rearranges to the more stable ozonide. Mechanisms for the formation of the ozonide have been proposed by Criegee, Leffler and Milas. Of these, the most widely accepted is the Criegee mechanism (6).

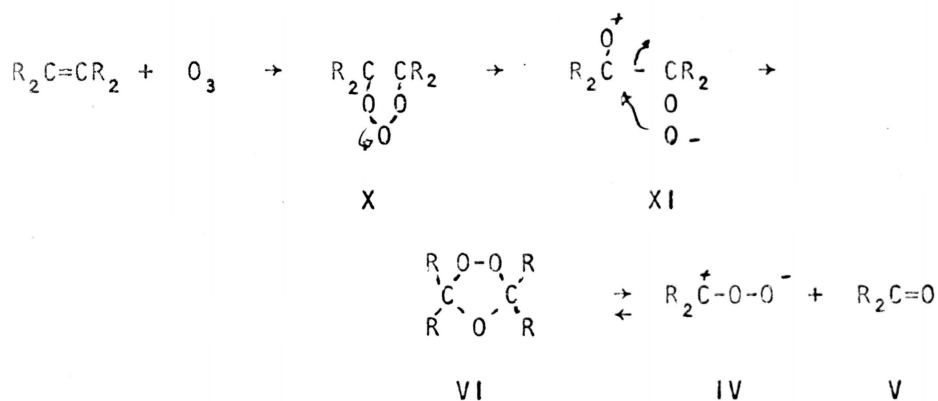


Criegee proposed that intermediate (II) of uncertain structure cleaved into two fragments, a zwitterion (IV) and a carbonyl containing fragment (V) through the unstable intermediate (III). The behavior of the zwitterion (IV) depended on its structure, the structure of the carbonyl containing fragment, and on the environment. The normal course of the reaction would be recombination with the carbonyl containing group to give the normal ozonide (VI) in inert solvents. In polar solvents such as aliphatic alcohols, Criegee proposed that the zwitterion combined with the solvent to give cyclic hydroperoxides.

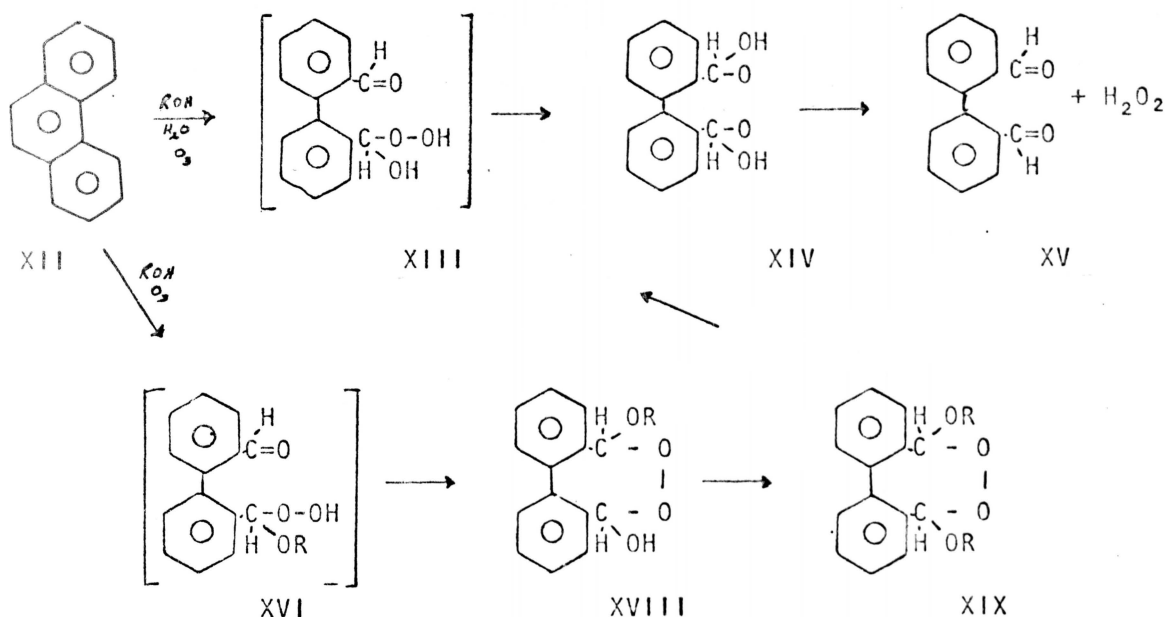
In further study, Bailey (7) determined using low temperature nuclear magnetic resonance spectroscopy, that the intermediate (II) which was not designated by Criegee was structure (X). Huisgen (8) proposed that ozone adds via a 2 + 3 cycloaddition as shown in structure (IX). A reverse 1,3 cycloaddition could give the fragments shown in structures (IV) and (V).



Milas (9) proposed a mechanism which involved the attack of ozone on the olefinic bond and a cleavage of the unstable intermediate (XI) and therefore rearrangement to the stable ozonide (VI) which is in equilibrium with the open zwitterionic forms (VI) and (V). According to this mechanism an ozonide is an intermediate in all ozonolyses and reaction with the carbonium ions and decomposition are the processes which form dimeric and polymeric peroxides.



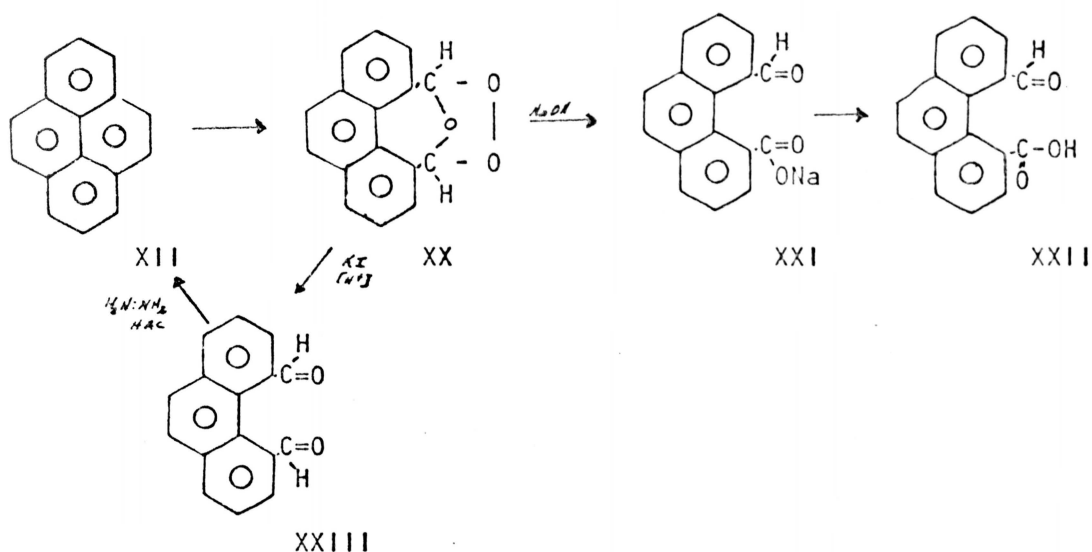
Prior to 1959, ozonations were invariably conducted under anhydrous conditions regardless of the solvent. Moriconi and co-workers (10) reported the ozonation of phenanthrene in anhydrous chloroform and acetic acid in 1955 and claimed the product obtained to be the first monomeric monoozonide to have been isolated in the arene series. Subsequent work by Bailey and Mainthia (11) in 1956 showed the material to be a polymer. In addition, Bailey (12) ozonized phenanthrene in anhydrous methanol and isolated hydroperoxide products which could be reduced with sodium iodide in acetic acid to 2,2'-biphenyldicarboxaldehyde with an 84% yield. Sturrock, Cline and Robinson (13) ozonized phenanthrene in mixtures of aliphatic alcohol and water in an attempt to bring about ozonation and hydrolysis concurrently. They found that water acts as a participating solvent in this reaction. The cyclic dihydroxyperoxide (XIV), analogous to the cyclic alkoxyhydroxy (XVIII) and dialkoxyperoxide (XIX) isolated by Bailey (12), was prepared and shown to be converted quantitatively to diphenaldehyde (XV) and hydrogen peroxide by gentle heating in acidic aqueous solution. Series of equilibria were postulated to explain the high yield of diphenaldehyde without the addition of a reducing agent.



Anthracene has been shown to be another example of the importance of water in the ozonation mixture. Yields of anthraquinone obtained directly as a precipitate were improved from approximately 35% in anhydrous methanol (14) to 73% in aqueous *t*-butyl alcohol by Sturrock, Cline and Robinson (15). In this instance the dicarbonyl compound is insoluble and therefore not available for further ozone attack. Subsequently Batterbee and Bailey (16) isolated 52% anthraquinone in 90% acetic acid-water mixtures without the aid of reducing agents.

The first report of the ozonation of pyrene was published in 1937 by Vollman (17). The reaction of ozone with pyrene to give 4-formyl-5-phenanthrenecarboxylic acid has been investigated repeatedly (18-21). In 1968, Sturrock and Duncan (4) isolated an intermediate from aqueous solutions of alcohols and characterized it as a monomeric monoozonide of pyrene. This was the first of this species to be authentically

identified in the arene series. They found that the monomeric monoozonide could be reduced with acidic potassium iodide to the 4,5-diformylphenanthrene and further that the oxidative fission could be reversed to regenerate pyrene by the application of the Bacon and Lindsay (23) reaction of hydrazine in boiling acetic acid. The monomeric monoozonide of pyrene rearranged readily upon gentle warming to give the 4-formyl-5-phenanthrene carboxylic acid as shown below.



Further work presented in the author's Master's Thesis (Texas Woman's University, August 1968) described the isolation of 1,10-dihydroxy-(4-tert-butyloxy)-1,4,7,10-tetrahydrobenzoxepino-(6,5,4-efg)benzodioxocin-8-one (XXXIII a), 1,4,10-trihydroxy-1,4,8,10-tetrahydrobenzoxepino(6,5,4-efg)benzodioxocin-8-one (XXXIII b) and the dinitrophenylhydrazone derivative of 2,2',6-triformyl-6'-biphenylcarboxylic acid (XXXVI). (These compounds will be referred to hereafter by the abbreviated names butoxyhydroxyperoxide (XXXIII a) and dihydroxyperoxide (XXXIIIb) respectively.

EXPERIMENTAL

The ozonation of the compounds described in the subsequent sections was carried out using a Welsbach T-408 ozone generator having a reaction vessel of the column type described in the Welsbach Basic Manual with the addition of a dry ice condenser. Because of the tendency of the hydrocarbon to settle below the fritted area of the gas inlet tube, the absorption apparatus was mounted on a magnetic stirrer. A "Teflon"-coated stirring bar revolving at moderate speed served to insure adequate homogeneity. The quantity of ozone absorbed in each experiment was determined using a potassium iodide trap and titration with sodium thiosulfate. Unless otherwise stated all experiments were carried out at room temperature and atmospheric pressure. The pyrene was Aldrich "puriss" grade (m.p. 147-154°) ground to acceptance by a 100 mesh sieve. All other chemicals employed were reagent grade. Microanalyses were carried out by the independent testing laboratory, Midwest Microlab, Inc., Indianapolis, Indiana, or in the TWU laboratory with a Perkin-Elmer-240 Elemental Analyzer. All melting points were determined with a Nalge Precise Melting Point Apparatus or an Electrothermal Capillary Melting Point Apparatus with standardized thermometers.

A total of more than 200 individual ozonation experiments was made, however the primary purpose of many was the preparation of pure monomeric monoozonide of pyrene which can only be prepared free of pyrene by carrying the reaction to completion.

A. Ozonation of Pyrene.

Typical experiments of the ozonation of pyrene involved the use of 5 grams of pyrene, 140 ml. of acetone or t-butyl alcohol and 70 ml. of water. The solution was treated with a stream of ozonized oxygen

containing 1.73 g. of ozone per cubic foot at a rate of 0.006 cubic feet per minute. (See chart 6, page 23, for structures.)

1. Ozonation of Pyrene in t-Butyl Alcohol-Water. The ozonation of pyrene in t-butyl alcohol allowed the isolation of the monomeric mono-ozonide as described by Sturrock and Duncan (4). The butoxy-hydroxyperoxide (XXIII) was precipitated by the addition of one gram of sodium chloride after dilution of the aqueous filtrate to a volume of 1000 ml. as described by Cravy (23). Elemental Analyses corresponded to a mixture of (XXXIII) and (XXXIV).

Elemental Analysis: Calculated for $C_{20}H_{20}O_7$: (XXXIV)

Carbon 64.5 Hydrogen 5.3 Oxygen 30.1

Calculated for $C_{20}H_{20}O_6$: (XXXIII)

Carbon 67.5 Hydrogen 5.6 Oxygen 26.9

Found:

Carbon 66.11 Hydrogen 5.40 Oxygen 26.9

a. Decomposition of the butoxy-hydroxyperoxide (XXXIII and XXXIV). Boiling this compound in acidic aqueous t-butyl alcohol produced a red syrup. Extraction of the red material with chloroform gave white crystals which melted at 170-5°. Nuclear magnetic resonance spectroscopy examination showed the presence of 2,2',6,6'-biphenyltetracarboxaldehyde (XXXV) and 2,2',6-triformyl-6'-biphenylcarboxylic acid (XXXVI).

b. Aqueous filtrate. The extraction of the aqueous filtrate with chloroform yielded several crops of crystals with melting points varying from 169° to 192°. Mass spectrometric examination of the material showed it to be a mixture of 2,2',6,6'-biphenyltetracarboxaldehyde (XXXV), 2,2',6-triformyl-6'-biphenylcarboxylic acid (XXXVI) and 2,2',6,6'-biphenyltetracarboxylic acid (XXXVII). (See section E and appendix.)

2. Ozonation of Pyrene in Acetone-Water.

a. Monomeric monoozonide of pyrene (XXX). The ozonide was recovered after ozonation of pyrene in acetone-water mixtures by allowing the acetone to evaporate at room temperature. As the concentration of acetone decreased, the ozonide precipitated slowly and was removed from the aqueous solution remaining by filtration with suction. This ozonide has been shown to have the same structure as the ozonide isolated by Sturrock and Duncan (4) from t-butyl alcohol and water. Identification was by infrared spectra (see appendix), active oxygen determinations using potassium iodide and acetic acid and conversion to 4-formyl-5-phenanthrenecarboxylic acid (XXXVIII) in warm dilute base with subsequent acidification. The ozonide, which was readily reduced with potassium iodide and acetic acid, could not be reduced with dimethyl sulfide in acetone solution upon stirring for approximately two hours. Only 4-formyl-5-phenanthrenecarboxylic acid (XXXVIII) was found.

b. Aqueous Filtrate. The aqueous solution obtained by the filtration of the ozonide gave a red paste on drying. Treatment of the red material with chloroform gave a light yellow solution. White crystals with a broad melting point in the range of 167° to 202° were obtained upon removal of the chloroform by boiling at atmospheric pressure and addition of a small amount of water. The best yield was 46% based on pyrene. Mass spectrometric examination of the crystals showed a mixture of the 2,2',6,6'-biphenyltetracarboxylic acid (XXXVII), 2,2',6-triformyl-6'-biphenylcarboxylic acid (XXXVI) and 2,2',6,6'-biphenyltetracarboxaldehyde (XXXV). Exhaustive fractional recrystallization of the mixture with water gave the 2,2',6,6'-biphenyltetracarboxaldehyde in 9% yield. m.p. 163-4°; literature 162-3° (18).

Elemental Analysis: Calculated for $C_{16}H_{10}O_4$:

Carbon 72.18 Hydrogen 3.76 Oxygen 24.06

Found:

Carbon 72.08 Hydrogen 3.81

Carbon 72.02 Hydrogen 3.77 Oxygen 23.90

Treatment of the pure 2,2',6,6'-biphenyltetracarboxaldehyde with hydrogen peroxide in aqueous solution increased the melting point from 164° to 181° .

Dimethyl sulfide reduction of the aqueous solution obtained from filtration of the ozonide substantially increased the yield of the 2,2',6,6'-biphenyltetracarboxaldehyde. The yield was 24% estimated by comparison of the results of mass spectrometry.

B. Ozonation of the Monomeric Monoozonide in Acetone-Water.

Typical experiments of the ozonation of the monomeric monoozonide of pyrene used 0.5 g. of ozonide, 70 ml. of acetone and 40 ml. of water. A red syrup formed when the acetone was removed by boiling at atmospheric pressure. White crystals with a melting point of 195° were obtained by extraction with chloroform and subsequent removal at atmospheric pressure. These crystals gave an immediate dinitrophenylhydrazine derivative in aqueous solution. Comparison of the infrared spectrum of the crystals obtained by the ozonation of the ozonide in acetone-water with the spectrum of the crystals obtained by the ozonation of the ozonide in t-butyl alcohol showed the same multiple absorption in the 5.7 to 6 μ m range.

Ozonation of the monomeric monoozonide for extended periods of time gave only the 2,2',6,6'-biphenyltetracarboxylic acid. m.p. 390° (Decomp.); literature 390° (Decomp.), (17). (XXXVII)

Elemental Analysis: Calculated for $C_{16}H_{10}O_8$:

Carbon 58.18 Hydrogen 3.03 Oxygen 38.79

Found:

Carbon 58.20 Hydrogen 2.96

C. Ozonation of the Monomeric Monoozonide with Reductive Treatment of Dimethyl Sulfide.

Approximately one-half gram samples of monomeric monoozonide were ozonized in 70 ml. of acetone and 40 ml. of water. The entire ozonation product was treated with 7 ml. of dimethyl sulfide. The acetone and dimethyl sulfide were removed by vacuum evaporation and the resultant aqueous solution was extracted with chloroform. When the chloroform was removed, white crystals were obtained which were shown to be 2,2',6,6'-biphenyltetracarboxaldehyde. The yield was 65.8%. m.p. 162-4°; literature 162° (18).

Elemental Analysis: Calculated for $C_{16}H_{10}O_4$: (XXXV)

Carbon 72.18 Hydrogen 3.76 Oxygen 24.06

Found:

Carbon 72.05 Hydrogen 3.66

The mass spectra and nuclear magnetic resonance spectra described under section E confirm the identification.

D. Ozonation of 4-Formyl-5-phenanthrenecarboxylic Acid Reduction with Dimethyl Sulfide.

The compound 2,2',6-triformyl-6'-biphenylcarboxylic acid was isolated from the ozonation of 0.3 g. of 4-formyl-5-phenanthrenecarboxylic acid in 70 ml. of acetone and 40 ml. of water when reduced with dimethyl sulfide. The 2,2',6-triformyl-6'-biphenylcarboxylic acid was separated from the unreacted starting material by chloroform extraction.

This compound has not been previously reported in the literature.

m.p. 199-200°.

Elemental Analysis: Calculated for $C_{16}H_{10}O_5$: (XXXVI)

Carbon 68.08 Hydrogen 3.54

Found:

Carbon 67.90 Hydrogen 3.45

The 2,2',6-triformyl;-6'-biphenylcarboxylic acid obtained by the ozonation of 4-formyl-5-phenanthrenecarboxylic acid was shown to be identical to that obtained from the ozonation of pyrene by infrared spectrometry, mass spectrometry and nuclear magnetic resonance spectrometry.

E. Spectroscopic Studies on Ozonation Products of Pyrene and Pyrene Monoozonide.

The following instruments were used under the conditions outlined in examination of the products obtained by the ozonation of pyrene and pyrene monoozonide.

1. Infrared Spectra

The infrared spectra were recorded on a Beckman IR-5 spectrophotometer. The samples were prepared as potassium bromide pellets by a Carver Laboratory Press Model K. No effort was made to maintain anhydrous conditions in the sample compartment. Concentrations of sample were varied in the pellet to obtain the best overall spectra. Representative spectra are presented in the appendix.

2. Ultraviolet Spectra

The ultraviolet spectra were obtained on a Cary Model 15 spectrophotometer using cylindrical one-centimeter silica cells. Concentrations employed varied between 3.2×10^{-3} and 6×10^{-5} molar in all solvents used. Plots of the spectra are presented in the appendix.

3. Nuclear Magnetic Resonance Spectra

The nuclear magnetic resonance spectra were obtained from a Varian A-60-A spectrometer. Tetramethylsilane was used as an internal reference for the determination of chemical shifts. Operating conditions and solvent employed are recorded on the individual spectra in the appendix.

4. Mass Spectra

The mass spectra were recorded on a Consolidated Electrodynamics Corporation (CEC) single-focus mass spectrometer model 21-104 with the following operating conditions.

Inlet system temperature: 170°

Source temperature: 250°

Ionizing voltage: 70 ev

Anode current: 10 microamps

Accelerating voltage: 3400 volts-nominal

Magnet current: 7.3 amps

Slit width; 4 mil

Electrostatic scanning rate: Position 9

Recording chart rate: 1/4 in/sec.

Detector: electron multiplier

Sample introduction was through the CEC Direct Inlet Probe (No. 285700). The temperature of the probe rose slowly from ambient to about 100° if the source temperature was initially at 250°. From this point, additional heat was supplied to the probe heater to raise the sample temperature to as high as 300°. The object of the temperature increase was to provide a form of temperature-programmed "distillation" of compounds of differing volatility. The spectra was scanned periodically.

Table I
 Ultraviolet Absorption of Monomeric Monoozonide
 of Pyrene (XXX)

λ max	ϵ max
354 nm	1.52×10^2
336	9.27×10^3
320	6.81×10^3
299	1.02×10^4
262	9.27×10^4

Varying the solvent by the use of ethanol, chloroform, acetonitrile, cyclohexane and aqueous sodium hydroxide did not cause the position of λ_{max} nor the values of ϵ_{max} to change. Since no effect was observed with change in solvent polarity, exact transitional assignments were not possible. It is probable that the bands at 299 and 262 nm are aromatic absorptions of the phenanthrene system. Some loss of resolution did occur in the aqueous sodium hydroxide solution but it is believed that this is a feature of the medium rather than the structure involved. The spectra obtained in all solvents showed unusual detail and resolution. It was therefore concluded that the molecule has a very rigid structure and a small number of vibrational states possible. Gentle heating of the basic solution of the ozonide followed by cooling to room temperature gave a solution whose spectrum was identical to that of the 4-formyl-5-phenanthrenecarboxylic acid. (XXXVIII)

Table 2
 Ultraviolet Absorptions of 4-Formyl-5-phenanthrene-
 carboxylic Acid (XXXVIII)

	λ_{max}	ϵ_{max}
Ethanol		
	362 nm	1.05×10^3
	346	1.03×10^3
	269	2.60×10^5
Aqueous Sodium Hydroxide		
	278 nm	2.7×10^4
	229	2.7×10^4

The 4-formyl-5-phenanthrenecarboxylic acid did not show the resolution found in the spectrum of the monoozonide of pyrene but like the ozonide, it did not show changes in the λ_{max} with change in solvent. The solvents used were ethanol, chloroform and acetonitrile. However, the spectrum of the 4-formyl-5-phenanthrenecarboxylic acid in aqueous sodium hydroxide solution showed drastic changes. The absorptions at 362 and 346 nm did not appear in the spectra at all and a broad plateau was obtained from 242 to 222 nm. Increasing the sensitivity and power allowed the detection of two λ_{max} at 278 nm and 229 nm. It is proposed that an equilibrium exists between the following structures all of which would be expected to have slightly different absorptions. Multiple absorptions of this type not resolved by the instrument could give the

the broad plateau observed in the spectrum.

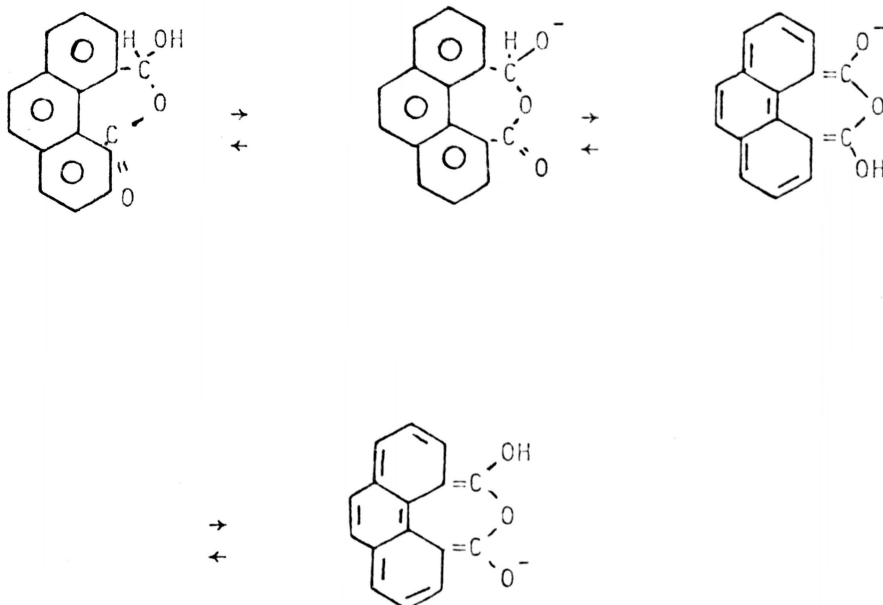
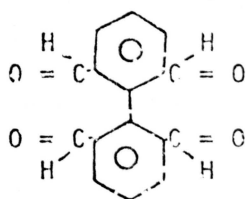


Table 3

Partial Mass Spectrum of 2,2',6,6'-Biphenyltetracarboxaldehyde:

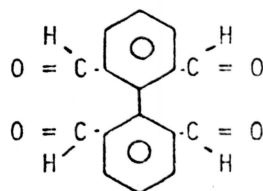


m/e	Percent Total Ionization	Relative Abundance
151	2.23	44.22
152	5.04	100.00
180	0.77	15.20
181	3.34	66.23
209	1.30	25.51
237	3.13	66.26
266 (P)	0.39	7.82

The appearance of the parent peak (P) corresponded to the calculated molecular weight of $C_{16}H_{10}O_4$. The complete spectra is presented in the appendix and a proposed pathway of the production of these ions is included in the discussion.

Table 4

Partial Mass Spectrum of 2,2',6'-Triformyl-6'-biphenylcarboxylic Acid:

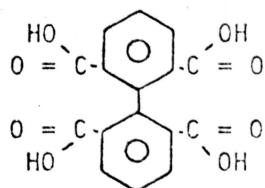


m/e	Percent Total Ionization	Relative Abundance
152	8.24	100.00
197	4.22	50.28
225	1.02	42.30
253	6.01	53.62
282 (P)	0.81	3.31

The observed parent peak (P) corresponded with the calculated molecular weight of $C_{16}H_{10}O_5$. The complete spectra is presented in the appendix and a diagram of the possible fragmentation pathway for the ions observed is presented in the discussion.

Table 5

Partial Mass Spectrum of 2,2',6,6'-Biphenyltetracarboxylic Acid:

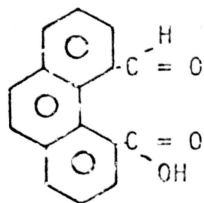


m/e	Percent Total Ionization	Relative Abundance
150	15.01	90.00
178	5.51	51.76
197	50.12	100.00
206	10.53	61.17
224	13.55	79.41
241	13.55	81.17
268	4.54	25.29
286	4.01	21.76
330 (P)	11.21	6.35

The observed parent peak (P) corresponded to the calculated molecular weight for $C_{16}H_{10}O_8$. The complete spectrum is presented in the appendix and a diagram of the proposed fragmentation pathway for the formation of the ions observed is presented in the discussion.

Table 6

Partial Mass Spectrum of 4-Formyl-5-phenanthrenecarboxylic Acid:



m/e	Percent Total Ionization	Relative Abundance
88	56.31	100.00
176	5.88	42.85
189	3.65	13.67
204	55.34	97.95
218	3.80	14.28
232	1.88	5.71
234	3.02	9.18
250 (P)	0.90	1.63

The observed parent peak (P) corresponded with the calculated molecular weight for $C_{16}H_{10}O_3$. The complete spectra is presented in the appendix and a proposed fragmentation pathway for the ions observed is presented in the discussion.

DISCUSSION

Although there are several mechanisms proposed for ozonation reactions as described in the historical section, there is still no complete agreement on which is correct. The theories proposed appear to have only one point in common which is that an initial adduct is formed when a molecule of ozone attaches itself to a double bond. Of these the molozone of Staudinger (Formula XXIX) is the most generally accepted. The various theories also seem to agree that when the initial adduct rearranges to form a simple ozonide, the five-member ring (Formula XXX) of Rieche (5) results. However there is considerable disagreement with respect to the manner in which the rearrangement occurs. The Criegee mechanism (6), which has gained widest acceptance, contends that the initial adduct immediately cleaves to discrete fragments, a "zwitterion" (Formula IV) and a carbonyl compound. Although it is nowhere clearly stated, it would seem that the Criegee fragmentation mechanism may have developed because at the time it was conceived no monomeric monoozonide had been isolated. While Criegee himself was the first to isolate a monomeric monoozonide in the alkene series (5), it was prepared in inert solvents. Since his theory predicts the formation of an ozonide in an inert solvent, it probably seemed to him that there was no need to modify his original thesis. In any event, the Criegee mechanism does not provide for the formation of an ozonide in protic solvents.

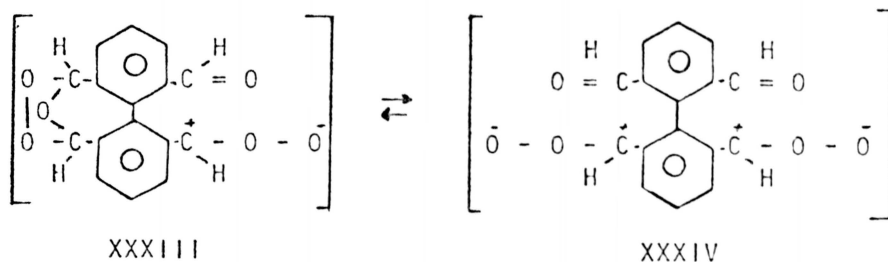
The Milas mechanism (9) postulates that the ozonide is formed by rearrangement of the molozone and that the ozonide may be in equilibrium with the zwitterion. Thus the Milas mechanism proposes that all ozonation reactions proceed through the ozonide. Since the first product

Upon reading the work of Sturrock and Duncan (4), Criegee (23) responded that the monomeric monoozonide of pyrene is formed from the zwitterion and aldehyde groups in the residual fixed phenanthrene system. Thus Criegee regards the formation of pyrene as an anomaly resulting from steric effects. His interpretation is open to criticism on the broad basis that the use of sterically hindered molecules is a common technique in mechanistic organic chemistry to permit the isolation of intermediates non-isolable in unhindered molecules. The equally plausible possibility that the ozonide actually precedes the zwitterion in accordance with the Milas mechanism must also be considered. This order of formation provides an explanation for the quantitative conversion of the monomeric monoozonide to the 4-formyl-5-phenanthrenecarboxylic acid by gentle warming. It is suggested that the ozonide formed the zwitterion but because of the proximity of zwitterion and aldehyde groups, it either does not react with the alcohol or water to form the series of peroxides isolable in the case of phenanthrene (15) or the reaction proceeds with such rapidity that they cannot be detected as in the case of anthracene (13).

Since the monoozonide is the sole source of the 4-formyl-5-phenanthrenecarboxylic acid (4), it would appear from the results of a great many experiments carried out in this and earlier work (4) and (23) that when the monoozonide concentration has reached approximately 30%, there is a competition for the ozone being supplied and the reaction of the ozonide and pyrene proceed at approximately the same rate. This explains why many investigators have been baffled in their attempts to improve the yield of 4-formyl-5-phenanthrenecarboxylic acid (18). It also explains why pure monoozonide can only be prepared by the introduction

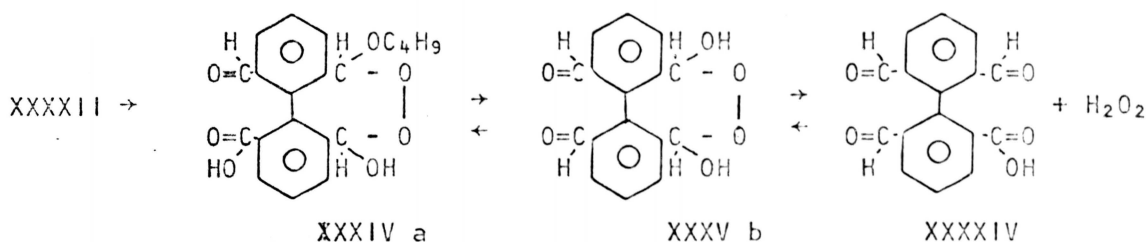
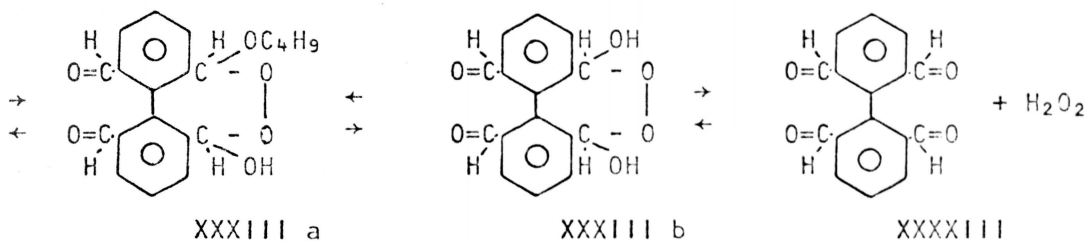
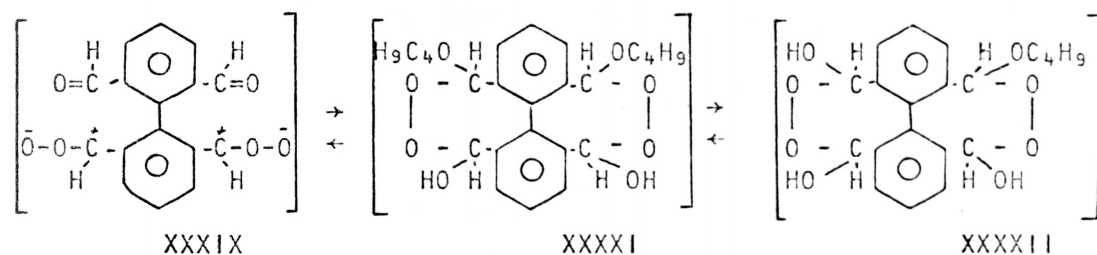
of 2.2 molar equivalents of ozone which is sufficient to react all the pyrene (4).

When the second molecule of ozone reacts with the pyrene monoozonide the fate of the ozonide ring becomes important. The original ozonide ring (XXX) could remain intact during attack of the 9,10-bond on the residual phenanthrene system or open to form the zwitterion. In the large number of experiments performed, there is no instance in which active oxygen determinations by the use of potassium iodide and acetic acid corresponded to a double ozonide. Furthermore the stereo-molecular model of the diozonide cannot be constructed. It is therefore proposed that the attack of the second molecule of ozone destroyed the original ozonide ring and the intermediate is structure (XXXIX).



Analogous with the reaction of ozone with phenanthrene, the zwitterion reacts with the solvent to form a series of equilibria between the alkoxyperoxide and the dihydroxyperoxide as shown in structures (XXXIX), (XXXXI), (XXXXII), (XXXIII a) and (XXXIII b).

Chart 8



It is believed that steric interferences prohibit the isolation of the dibutoxyhydroperoxide (XXXI) in aqueous t-butyl alcohol. The first isolable product is a cyclic butoxyhydroperoxide of a substituted biphenyl (XXXIII) and (XXXVI). The results of a series of elemental analyses of this product did not correspond to either the butoxyperoxide of biphenaldehyde (XXXIII) nor to the butoxyperoxide of biphenaldehyde acid (XXXIV). Best agreement was found to be with the calculated values of the two. The zwitterion may have reacted with water, then rearranged to form the aldehyde acid or split out hydrogen peroxide to give the

dialdehyde. The 2,2',6,6'-biphenyltetracarboxaldehyde is formed from the dihydroxyperoxide of the biphenaldehyde (XXXIIIb) without the addition of reducing agents which is further analogous with phenanthrene (15). It is proposed that the addition of dimethyl sulfide destroys the hydrogen peroxide formed therefore shifting the equilibrium to allow the isolation of an increased yield of 2,2',6,6'-biphenyltetracarboxaldehyde (XXXXIII). The 2,2',6-triformyl-6'-biphenylcarboxylic acid (XXXXIV) is formed from (XXXIVb) in the same manner. Dimethyl sulfide is specific for active oxygen in hydroperoxides (24), does not attack the ozonide and certainly would not bring about the reduction of the 2,2',6-triformyl-6'-biphenylcarboxylic acid to increase the yield of 2,2',6,6'-biphenyltetracarboxaldehyde.

The foregoing postulations may represent an over simplification of the actual mechanism which could involve the rearrangement of the cyclic dihydroxyperoxide to the open chain hydroperoxides before reduction with dimethyl sulfide. The appearance of the accompanying acidic product in the case of pyrene (2,2',6,6'-biphenyltetracarboxylic acid) is readily explained by the fact that biphenaldehyde is unusually resistant to oxidation (17) whereas 4,5-phenanthrenedicarboxaldehyde is easily oxidized (4). The oxidation of phenanthrene and biphenyl polyaldehyde derivatives by ozone has been demonstrated by other workers (18, 19), who obtained 2,2',6,6'-biphenyltetracarboxylic acid (XXXVII) in 61% yield by the exhaustive ozonation of pyrene.

On the basis of the evidence presented, it is, therefore possible to argue logically that the isolation of the monomeric monoozonide from the products of ozonation of pyrene in aqueous media is not an anomalous reaction resulting from steric effects. Rather it appears that the

steric hindrance in pyrene has permitted the isolation of intermediate products which indicate the actual mechanism of the overall reaction and supports the Milas mechanism.

The use of mass spectrometry for identification of the products described above permits examination of spectra of compound types which have not been characterized previously by the instrument. Compounds capable of undergoing successive losses of aldehyde and acid functional groups in the 2,2', 6 and 6' positions of a biphenyl system lend themselves to the formation of intermediate rings in the fragmentation process. A suggested fragmentation pattern for the formation of the ions observed is presented in Charts 9, 10, 11 and 12 for 2,2',6,6'-biphenyltetracarboxaldehyde, 2,2',6-triformyl-6'-biphenylcarboxylic acid, 2,2',6,6'-biphenyltetracarboxylic acid and 4-formyl-5-phenanthrene-carboxylic acid. The pathways indicated for the formation of the various ions should be regarded as possible pathways and not as defined pathways. Emphasis must also be placed on the fact that observation of the presence of a given m/e does not allow structure assignment. Fragmentation patterns are proposed only for the loss of the functional groups since the biphenyl system fragmentation has been established by Natlis and Franklin (25). Examination of the spectra indicated agreement with their work in that the main fragment ions corresponded to the loss of one or two H atoms or to the loss of C_2H_2 , C_3H_3 and C_4H_4 groups. The spectra also showed a number of double charged ions in agreement with their data.

The pathways which are presented repeatedly involve McLafferty rearrangements, that is the formation of six member transition states. Loss of some aldehyde and acid functional groups appear to follow the fragmentation pathways proposed for benzaldehyde and benzoic acid (26).

Chart 9

Proposed Fragmentation Pathway for 2,2',6,6'-Biphenyltetracarboxaldehyde:

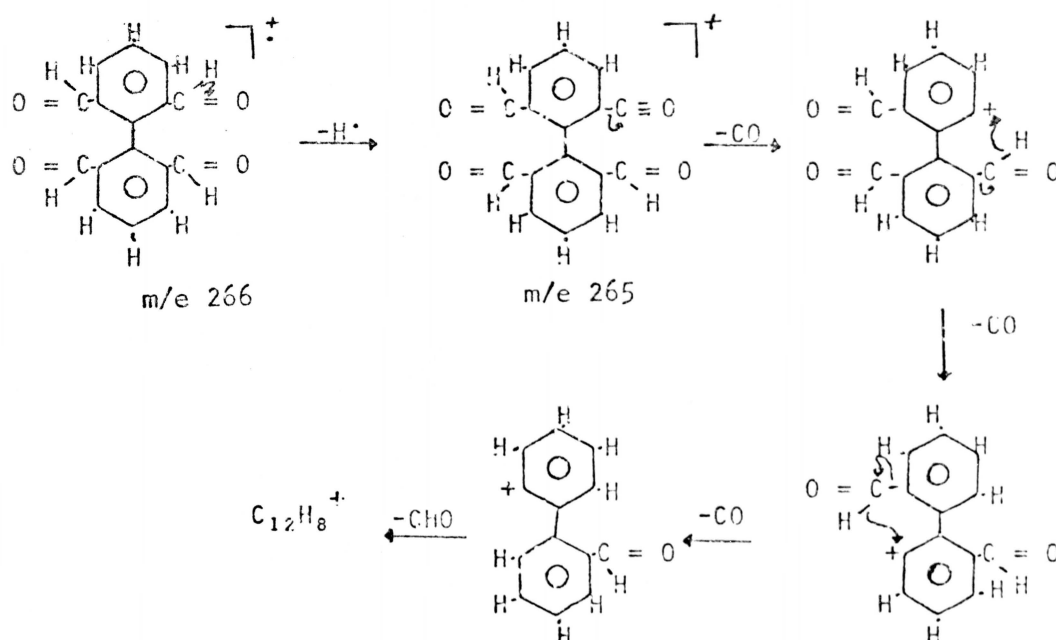


Chart 10

Proposed Fragmentation Pathway for 2,2',6-Triformyl-6'-biphenylcarboxylic Acid.

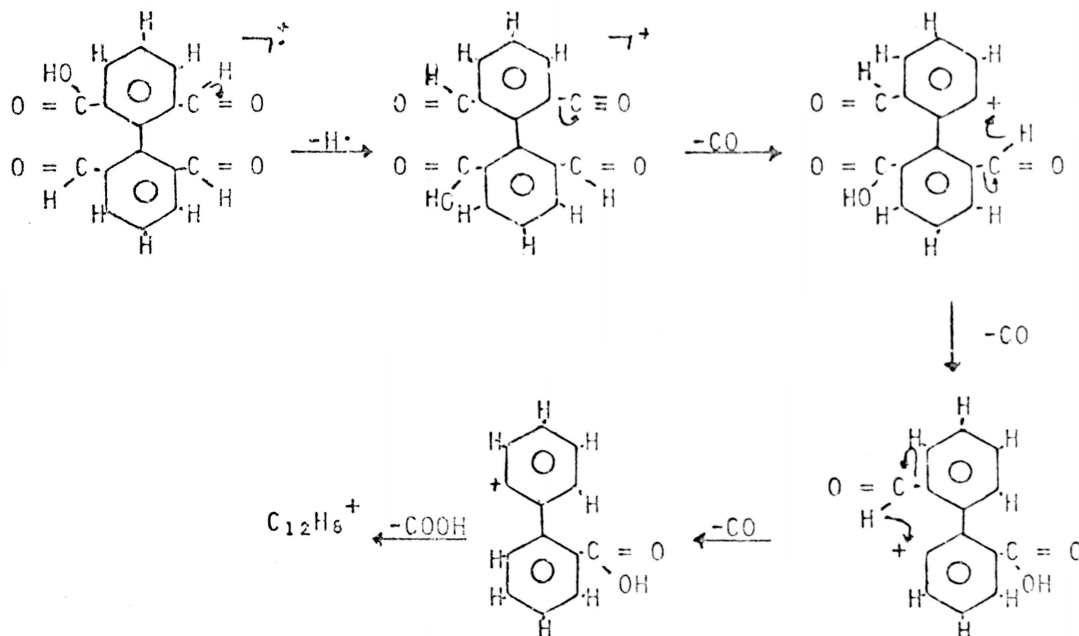
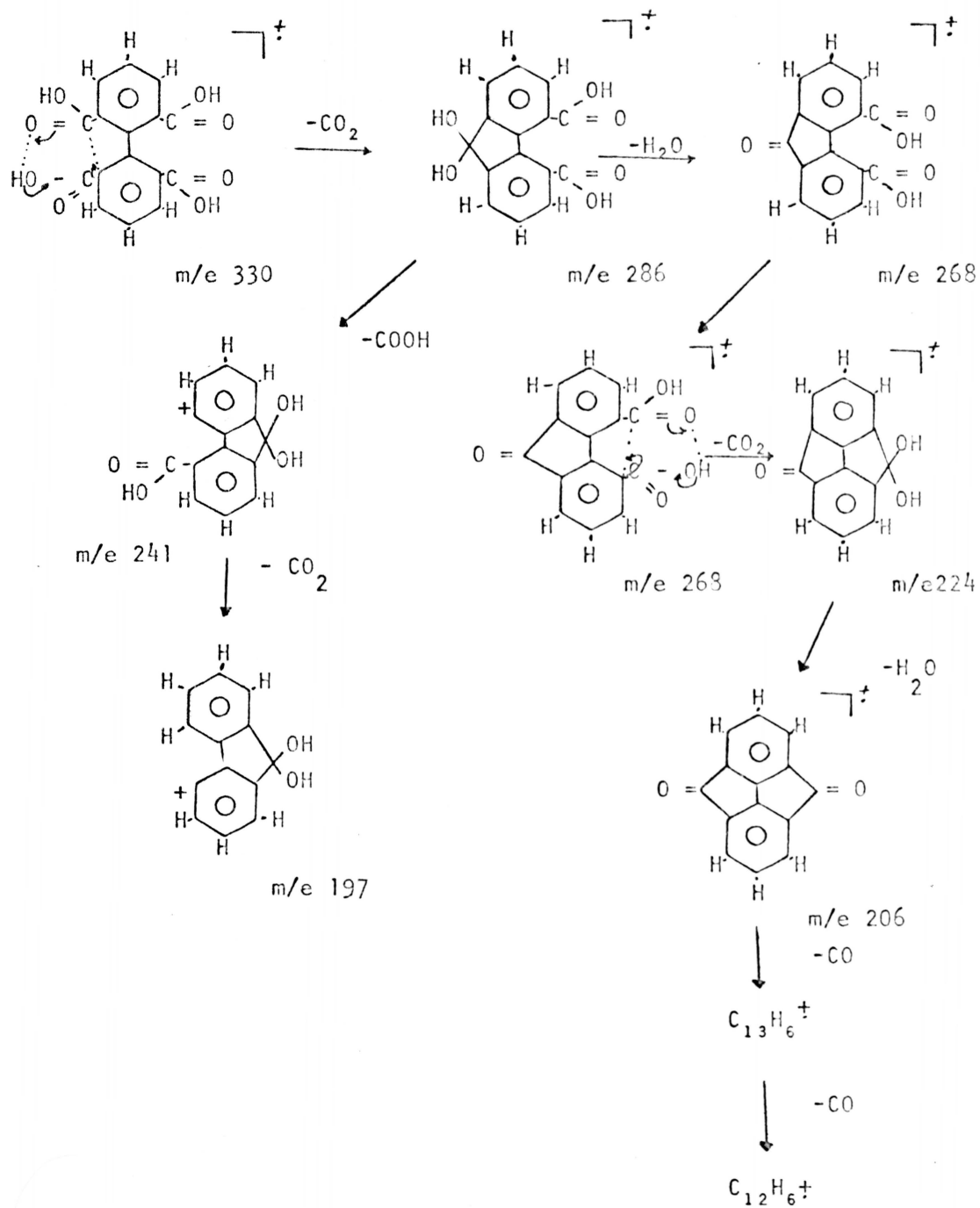
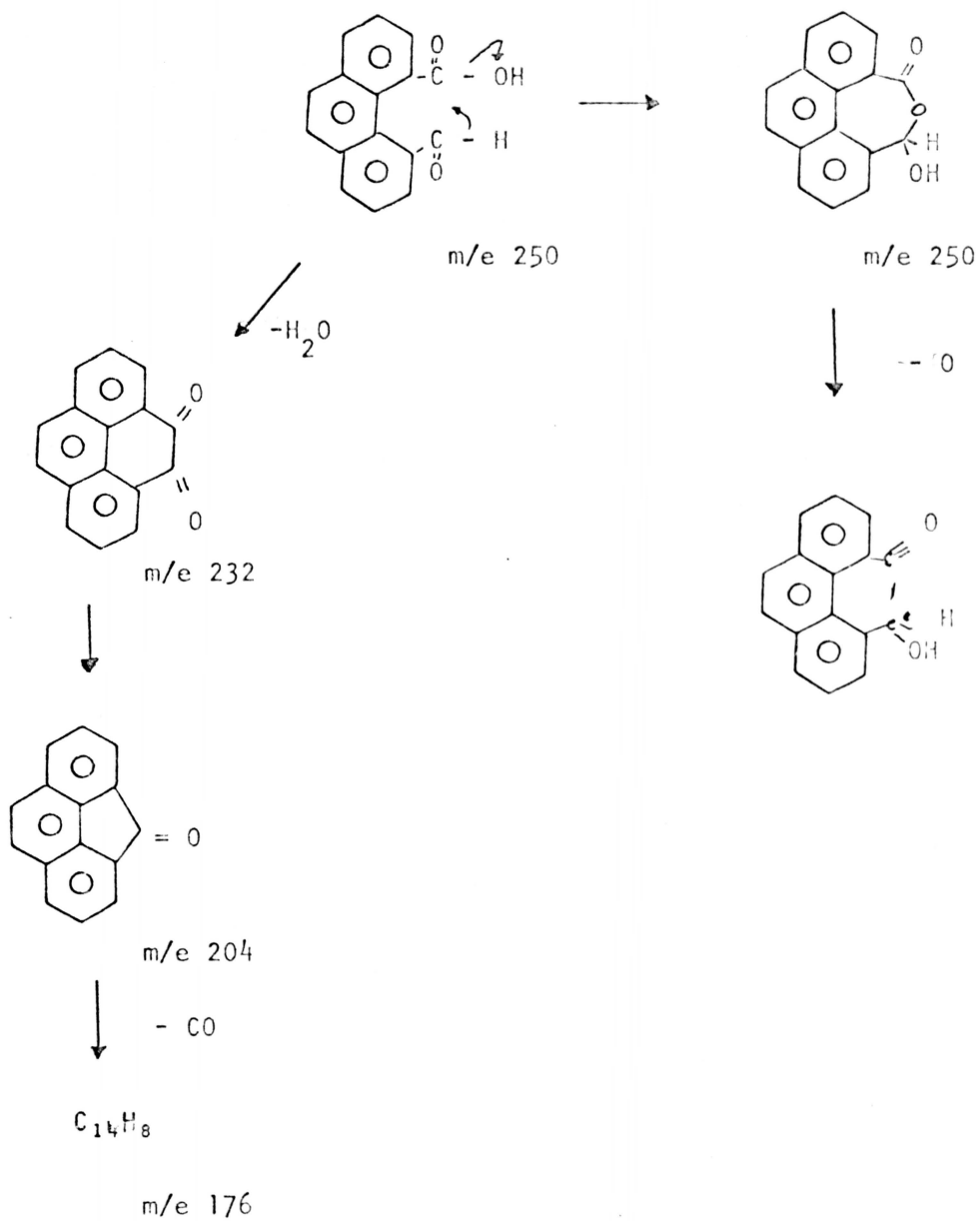


Chart 11

Fragmentation Pathway for 2,2',6,6'-Biphenyltetracarboxylic Acid:



Proposed Fragmentation Pathway for 4-Formyl-5-phenanthrenecarboxylic
Acid:



The appearance of metastable peaks at m/e 151.1, 236.8 and 208.8 are used as evidence to support the proposed pathway in the 2,2',6,6'-biphenyltetracarboxaldehyde. These peaks are the result of decomposition after near complete acceleration from the ion source, but before complete mass separation. The product ion from such a decomposition gives rise to a somewhat diffuse peak in the spectrum below its actual m/e . In the conventional, single-focusing mass spectrometer, the product ion, m_1 , from the decomposition of the precursor ion m_2 , is most likely to be found at mass m^* , where $m^* = \frac{m_1^2}{m_2}$ (26). Examination of the spectrum of fluorenone allows correlation of the fragmentation pathway from m/e 178 in the 2,2',6,6'-biphenyltetracarboxylic acid spectrum.

The synthesis of labeled molecules would be necessary for complete elucidation of the mechanism proposed.

SUMMARY

The widely accepted Criegee mechanism for the reaction of ozone with double bonds postulates that normal ozonides are formed from a zwitterion in inert solvents and that they are not formed at all in polar ("participating") solvents. The Milas mechanism, on the other hand, proposes that normal ozonides are formed in all ozonation reactions, that the ozonide is in equilibrium with the zwitterion and that in polar solvents the equilibrium is shifted away from the ozonide as a result of reaction of the zwitterion with the solvent.

It is proposed that this study of the ozonation of pyrene in aqueous solutions supports the Milas mechanism since the first product isolated is a monomeric monoozonide of pyrene in participating solvents and subsequent products isolated are formed from the zwitterion.

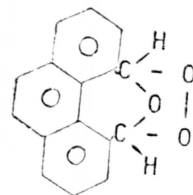
The results of the present study of the mechanism of the ozonation of pyrene do not represent the first challenge to the general applicability of the Criegee mechanism to ozonation reactions. It is, however, the first example of the inadequacy of the Criegee postulations when applied to the ozonation of polycyclic hydrocarbons.

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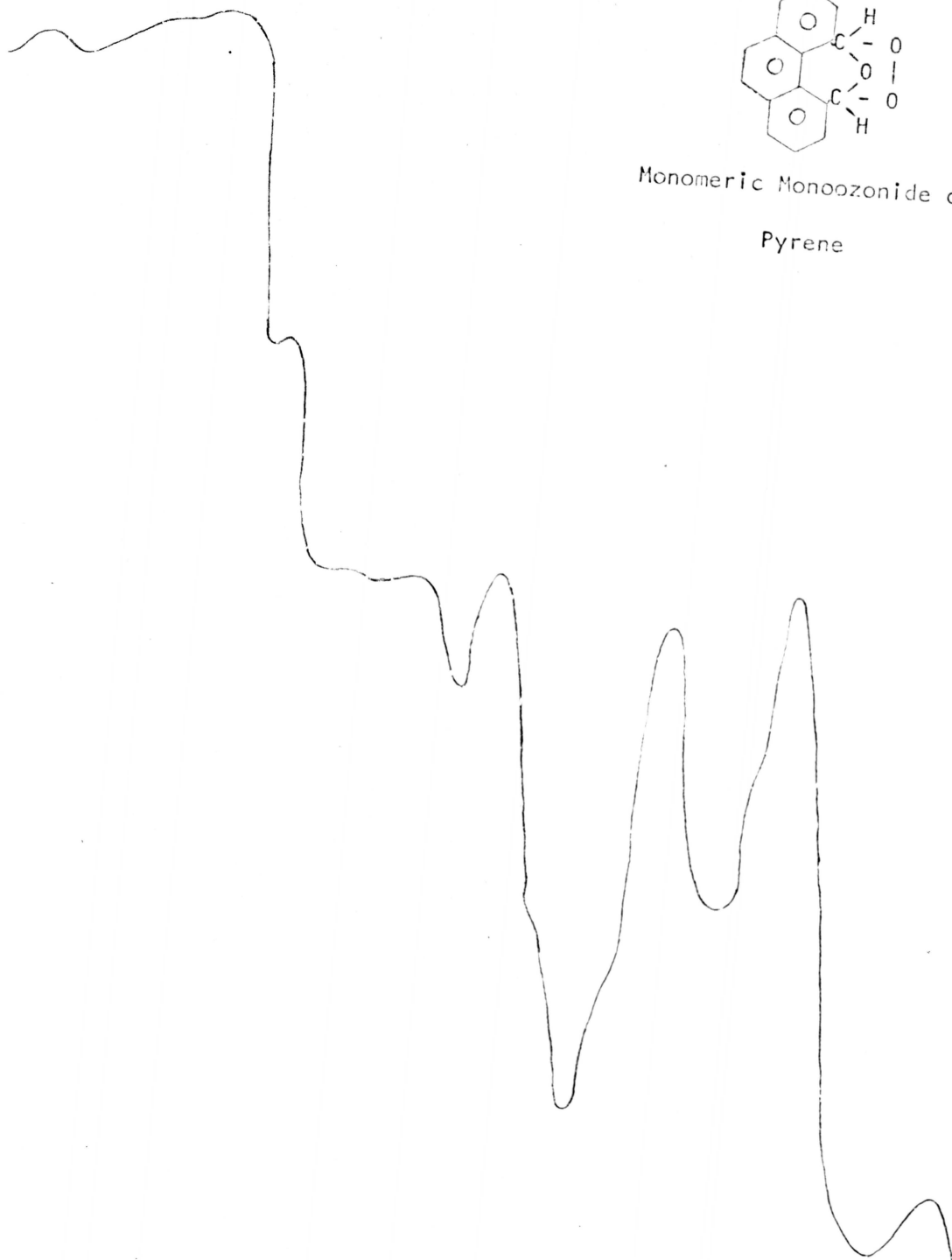
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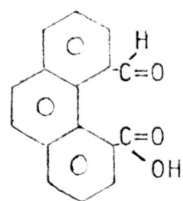
Plot of Ultraviolet Absorption Spectra



Monomeric Monoozonide of
Pyrene



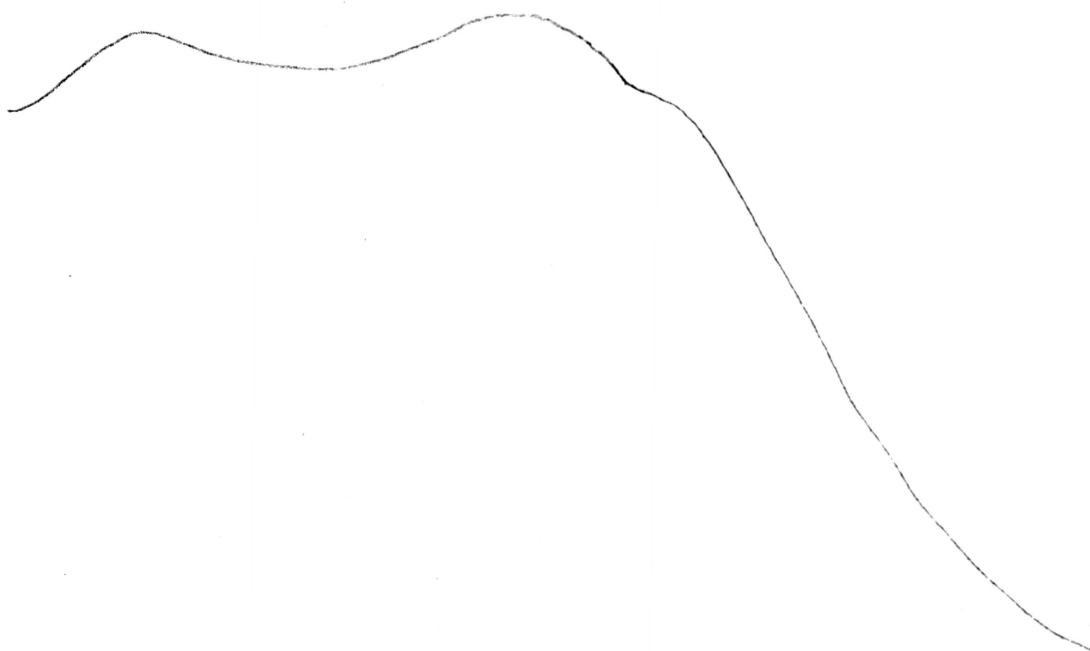
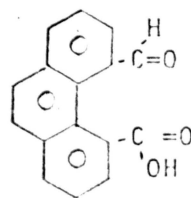
Plot of Ultraviolet Absorption Spectra



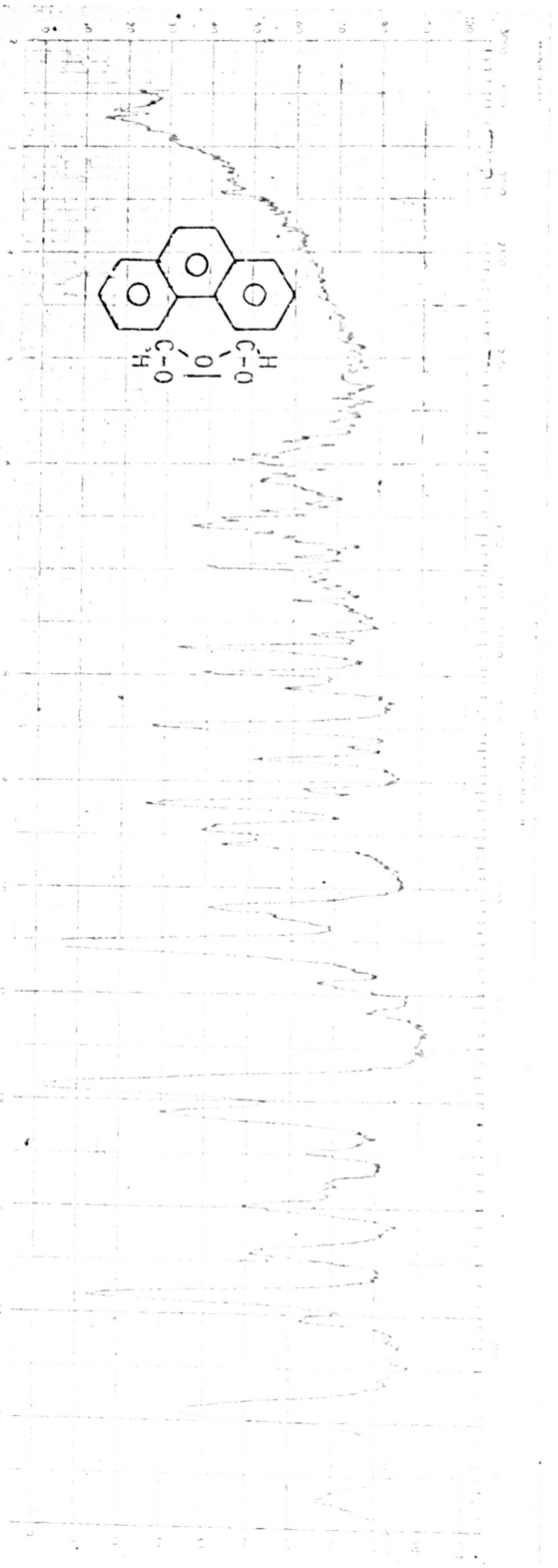
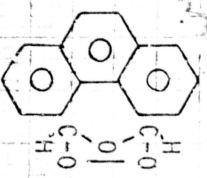
4-Formyl-5-Phenanthrene-
carboxylic acid

Plot of Ultraviolet Absorption Spectra

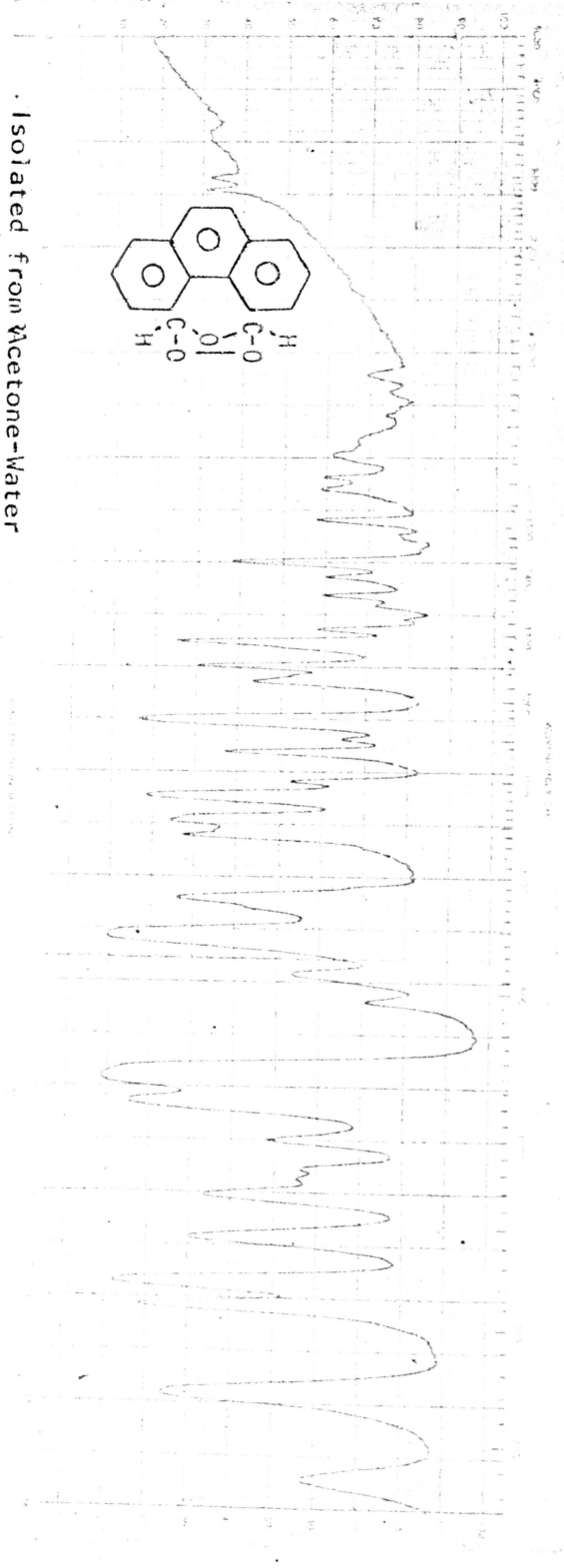
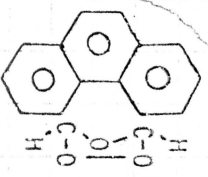
0.1 N Sodium Hydroxide

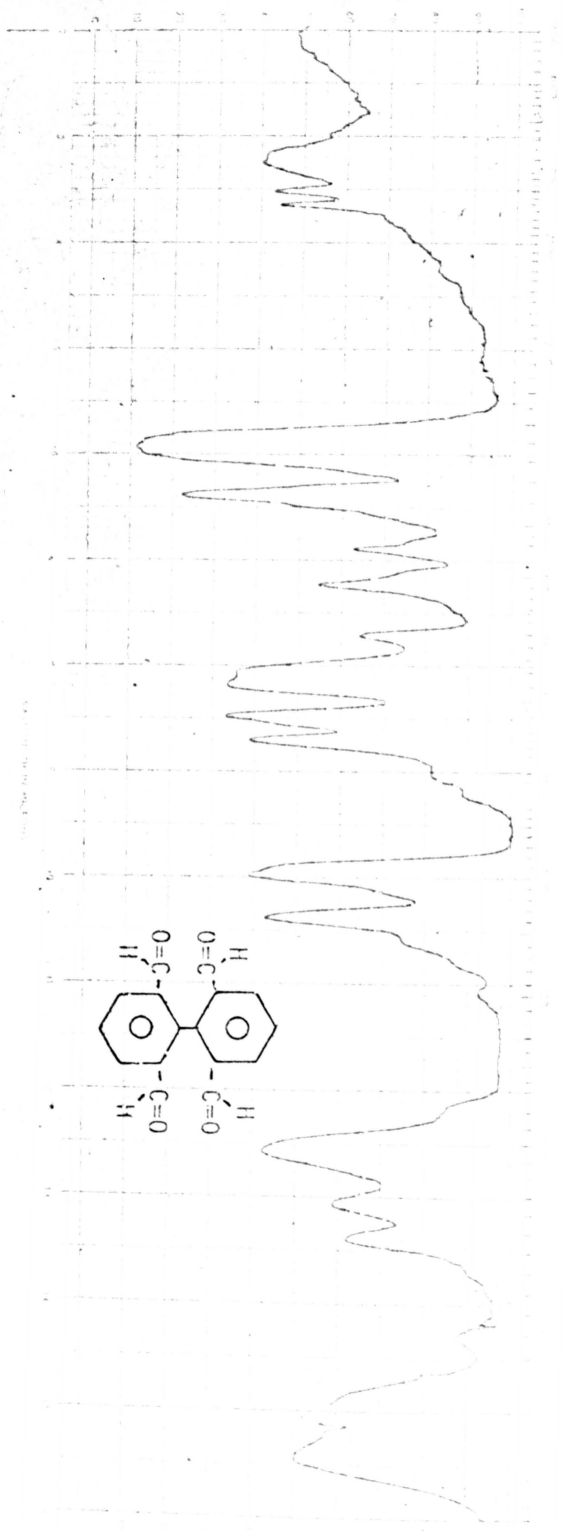
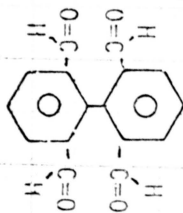
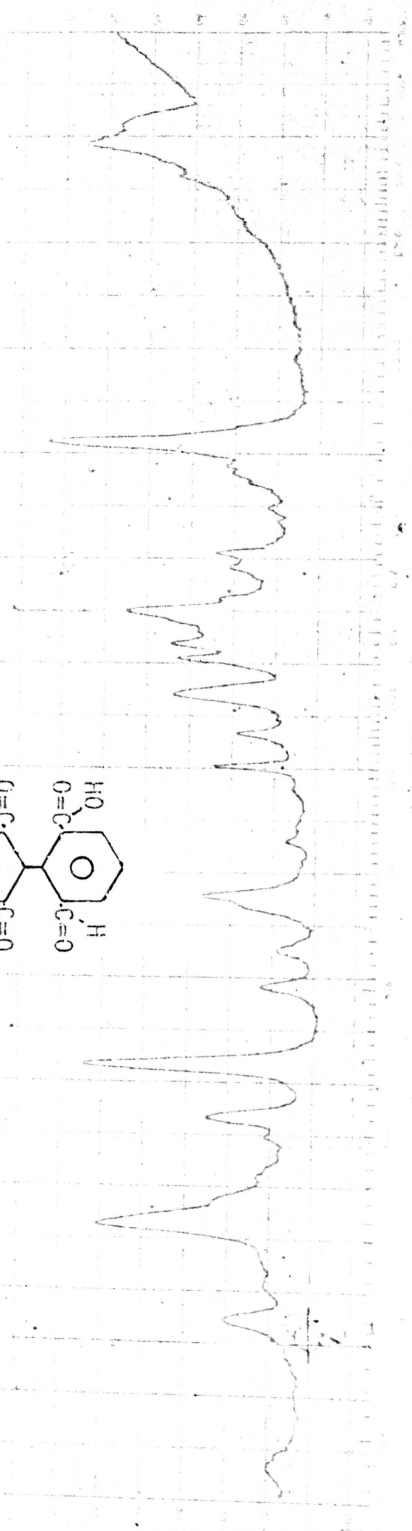
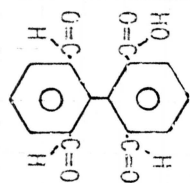


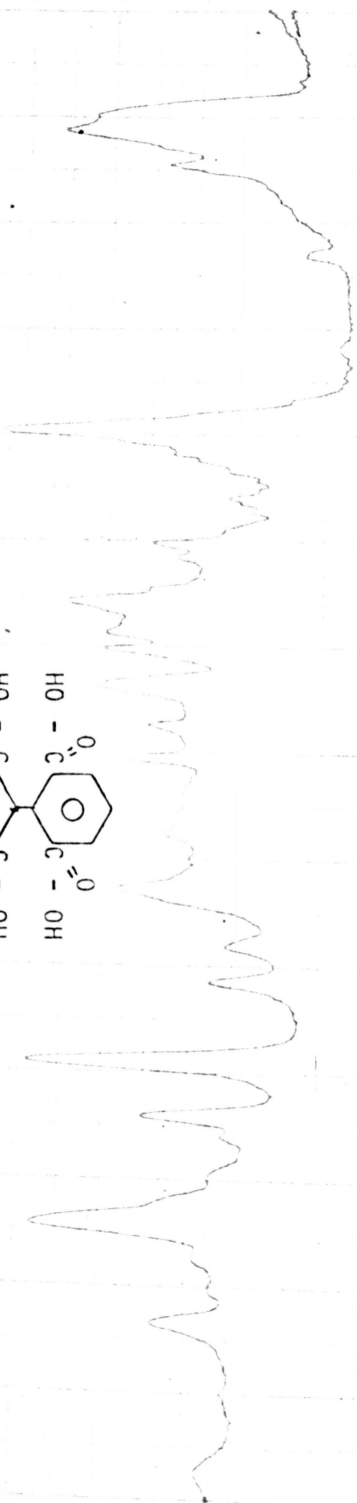
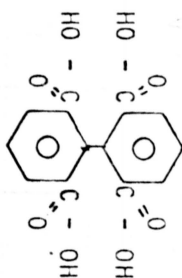
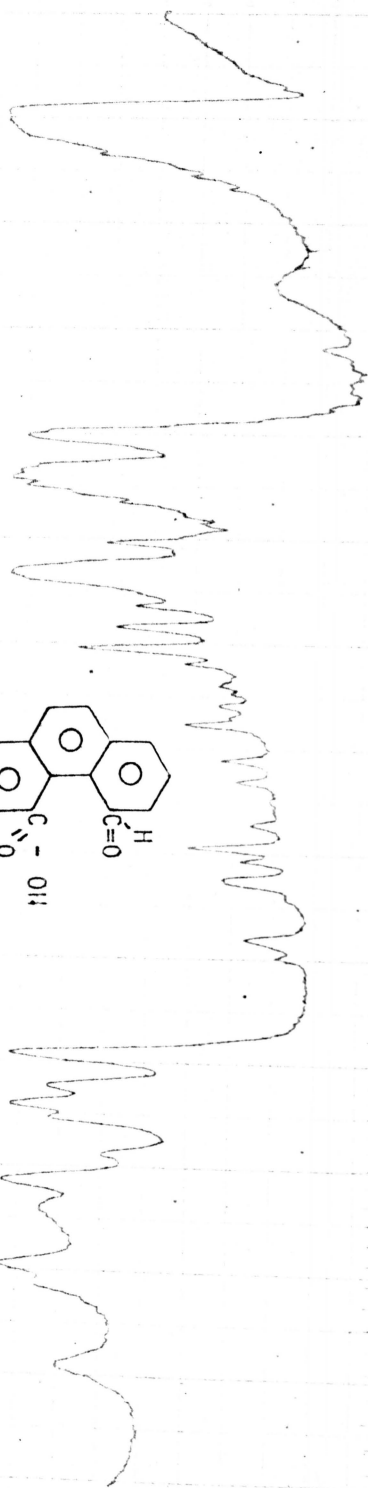
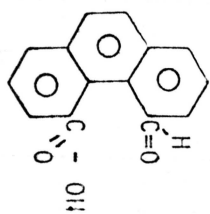
Isolated from β -butyl alcohol+Water

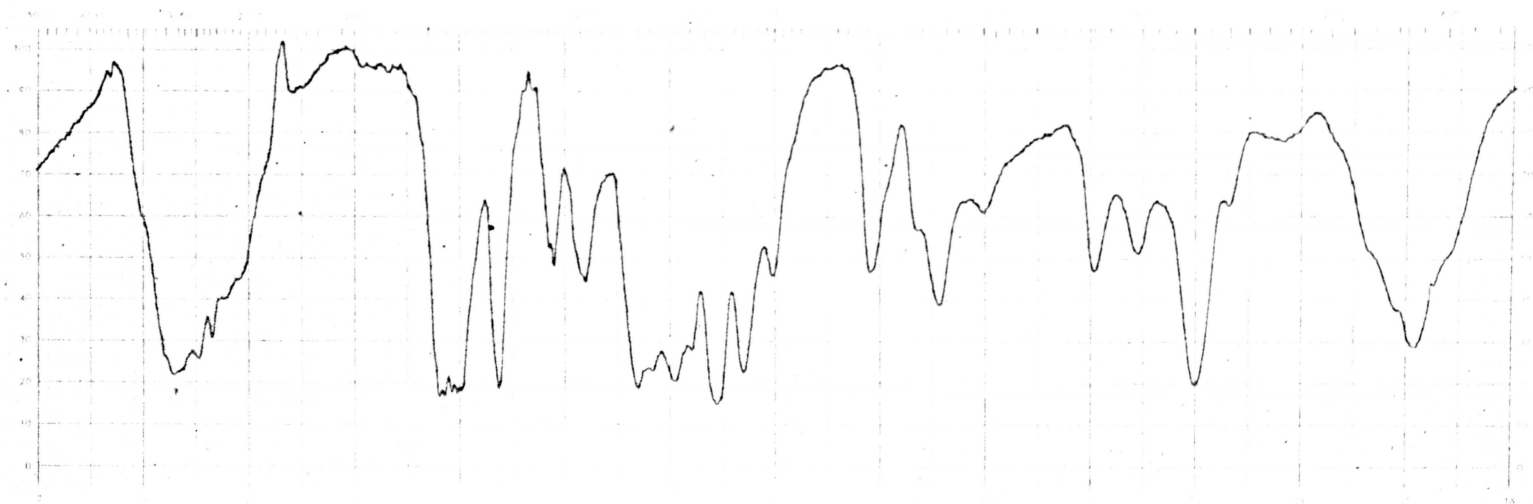


Isolated from Acetone+Water

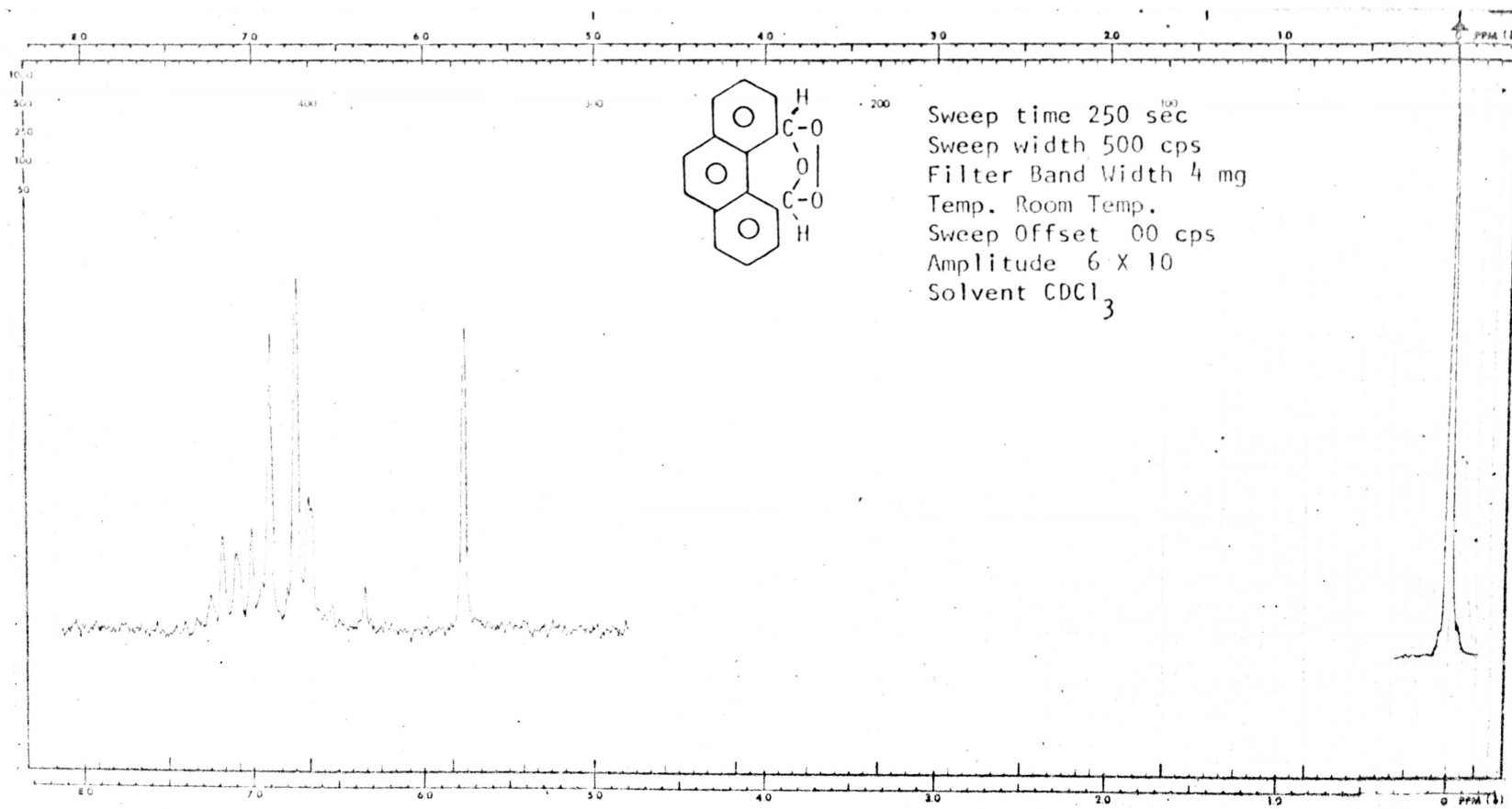


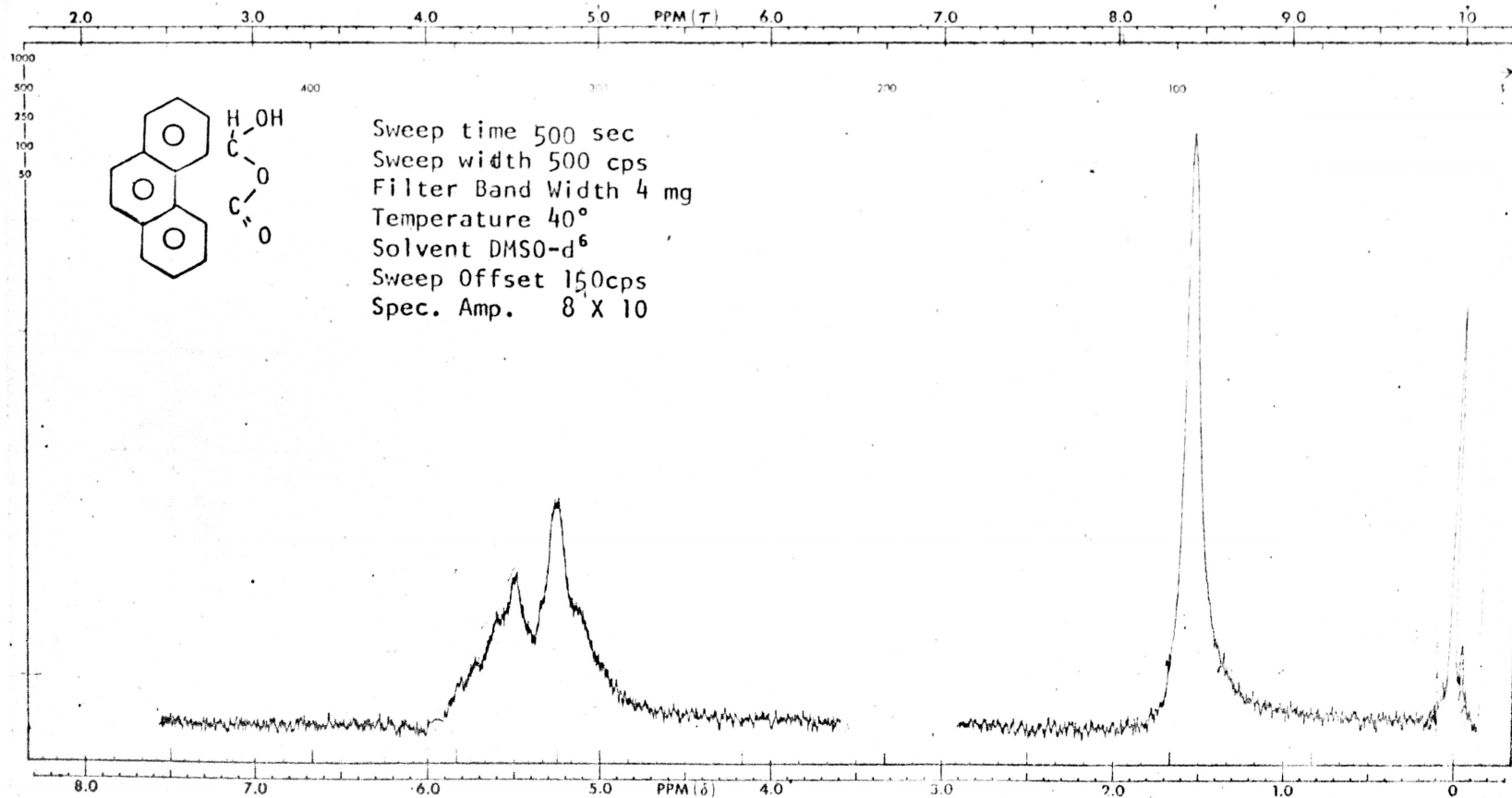


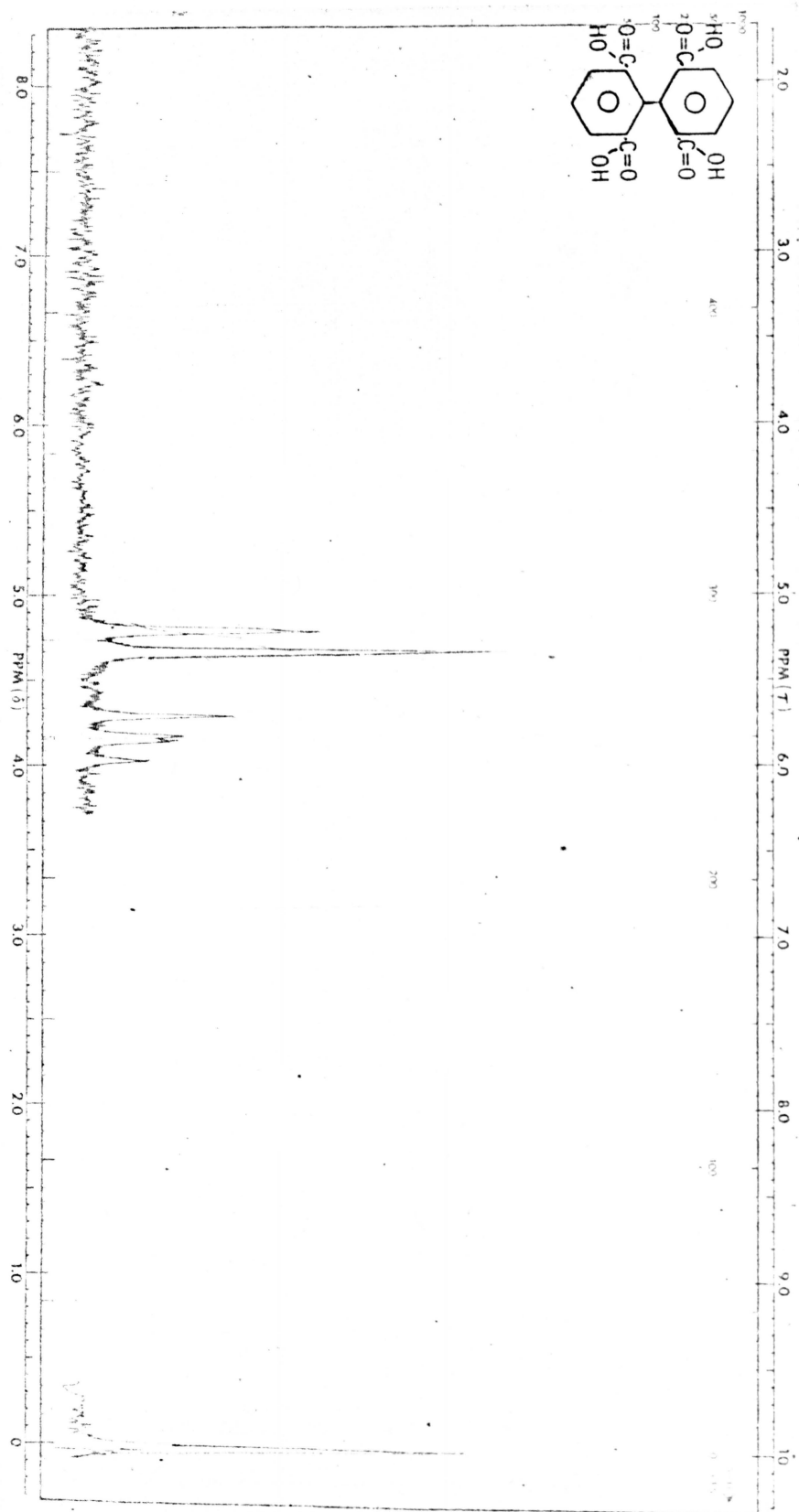


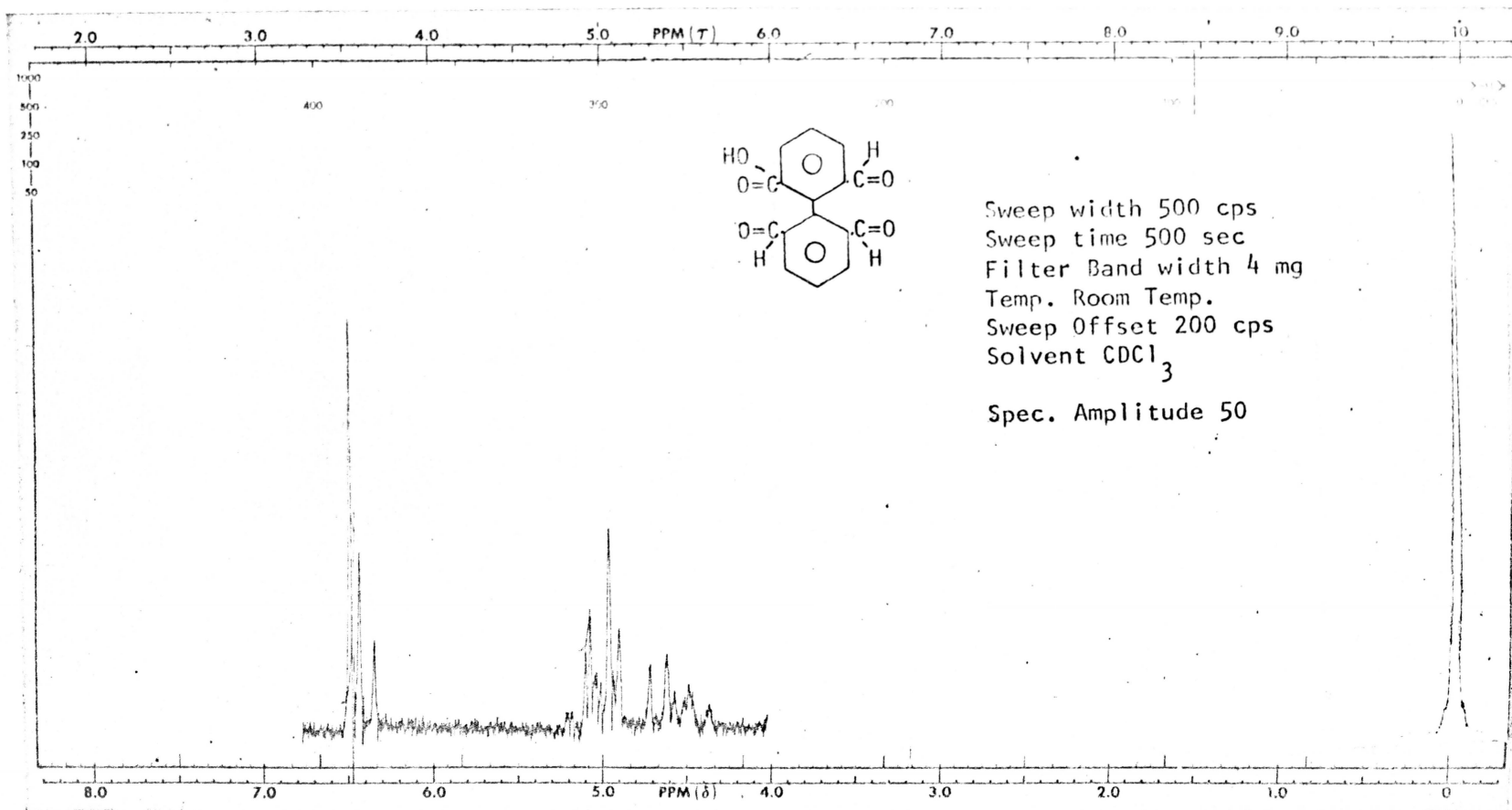


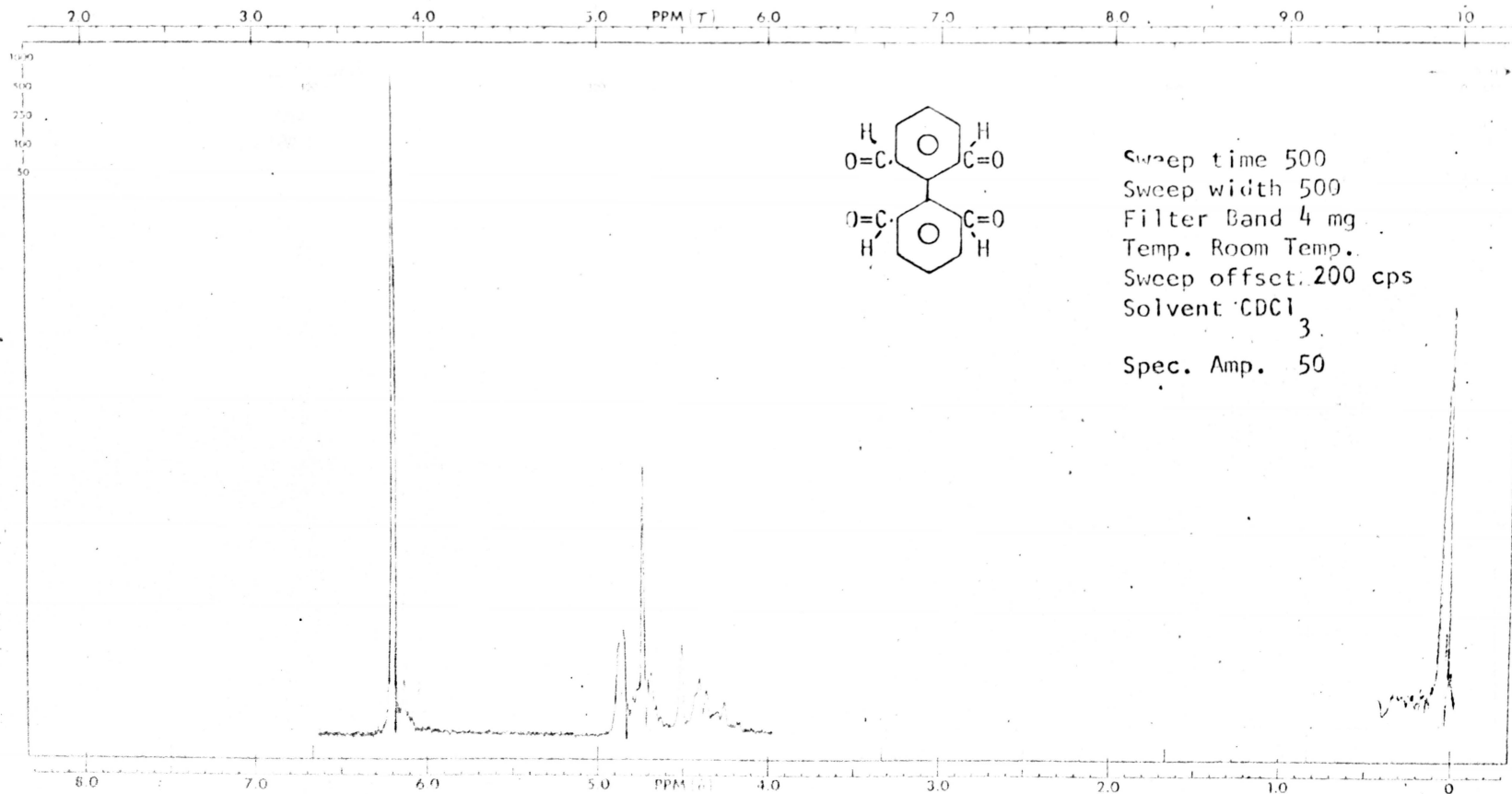
Mixture of 2,2',6,6'-biphenyltetracarboxaldehyde, 2,2',6-triformyl-6'-biphenylcarboxylic acid and 2,2',6,6'-biphenyltetracarboxylic acid.











ABSTRACT

Cravy, Betty Dozier

The Mechanism of the Ozonation of Pyrene- Ozonide-Zwitterion
Relationships

Directed by Dr. Murray G. Sturrock

Submitted for the Doctor of Philosophy Degree, December, 1970

The widely accepted Criegee mechanism for the reaction of ozone with double bonds postulates that normal ozonides are formed from a zwitterion in inert solvents and that they are not formed in polar ("participating") solvents. The Milas mechanism, on the other hand, proposes that normal ozonides are formed in all ozonation reactions, that the ozonide is in equilibrium with the zwitterion and that in polar solvents the equilibrium is shifted away from the ozonide as a result of reaction of the zwitterion with the solvent.

The isolation of pyrene monoozonide from ozonations conducted in polar solvents was not in accord with the Criegee mechanism. In response to Criegee's explanation that the formation of pyrene monoozonide is an anomaly resulting from steric effects, evidence has been adduced to show that subsequent reactions of the monoozonide with ozone must proceed through the zwitterion, a pathway that is again contrary to the Criegee mechanism.

Spectroscopic studies have been conducted on many of the ozonation products.

VITA

Betty Jean Dozier Cravy was born March 11, 1941, in Canton, Texas. She graduated from Canton High School, Canton, Texas in 1958 and from Tyler Jr. College in Tyler Texas in 1960. She received a Bachelor of Science from Stephen F. Austin State College in Nacogdoches, Texas in 1963 with a major in chemistry. In 1968 the Master of Science degree was granted by Texas Woman's University.

The author married Michael G. Cravy, June 15, 1963 and they have one daughter Carol Cravy, who is two years old.