THE UNIVERSITY OF MANITOBA

THERMAL DECOMPOSITION OF DIAZOIMINO COMPOUNDS

by

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ABSTRACT

In order to gain information about the formation of primary amine from the thermal decomposition of diazoimino compounds which was first reported by Dayal (10), the effect of various aromatic substituents on the yield of primary amine has been investigated in buffered aqueous media at elevated temperatures.

During the course of this investigation, it has become obvious that reaction pathways leading to products other than aromatic amine must be included in the tentative mechanism first proposed by Dayal (10). However, the results of this investigation have not shed any new light on the mechanism of formation of aromatic amine from the decomposition of diazoimino compounds.

ACKNOWLEDGMENTS

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I. INTRODUCTION

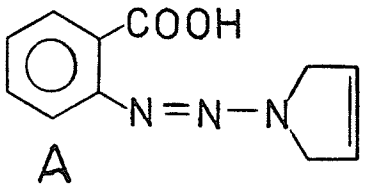
The importance of triazenes has long been recognized in the dyeing industry as a source of diazonium ions in the manufacture of an important class of water soluble dyes known as Rapidogens(32). Under acid conditions the triazenes decompose *via* an ionic pathway to give the corresponding diazonium salt which is subsequently coupled to a suitable coupling component of the Naphtol A S type (3-hydroxy-2-naphthanilides) to give the resulting dye. Another industrially important class of dyes are the aminoazo dyes. The latter are formed as products in the well known diazoamino rearrangement(32,19).

However, homolytic modes of decomposition are also known for triazenes of the type $Ar-N=N-NR_2$ and $Ar-N=N-NHR$ These compounds have been shown to possess the ability to initiate polymerization of a variety of monomers at temperatures in the neighbourhood of 100°C(11). The polymer industry also makes use of triazenes as blowing agents in the manufacture of foamed synthetic rubbers(32). Blowing agents are compounds capable of liberating gases on heating such as triazenes are capable of doing.

An additional and perhaps more important point of interest with regards to triazenes are their tumour inhibiting properties. About fifteen years ago, Clarke, Barclay and Rondestvedt(9) reported that certain aromatic triazenes exhibited inhibition of mouse Sarcoma - 180. More recently, several papers have appeared in the literature concerning the anti-leukemic and tumour inhibiting properties of triazenes(21,26,27,(28).

Recently, Dayal(10) reported another mode of decomposition for triazenes. He decomposed 1 g of 1-(2-carboxyphenyl)-3-pyrrolinotriazene (hereafter to be called A) in the presence of 50 ml. water at 40°C for

two days in an oil bath.



A

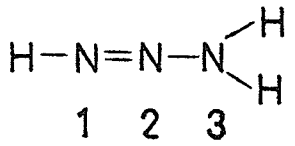
The product of decomposition was observed to be a dark solid material which after several recrystallizations from benzene yielded .2 g of a solid (melting point 145°C). The product was identified from its elemental analysis and its u.v. and i.r spectra to be anthranilic acid. However, he was unable to isolate any product originating from the imino portion of A.

To date, no other report of such a mode of decomposition of diazoimino compounds has appeared in the literature. We, therefore, wish to investigate this particular mode of decomposition and the factors which influence it.

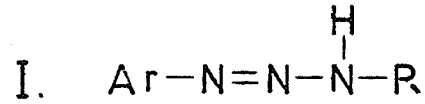
II. LITERATURE REVIEW

1. General

Triazene itself, is an unknown substance, but

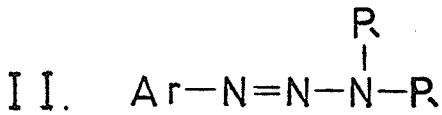


appropriate substitution of the various hydrogens forms the basis of the nomenclature for two important classes of derivatives. If the hydrogen on N_1 is replaced with an aryl group, and either of the N_3 hydrogens is replaced by either an aliphatic or aromatic group, the triazene in question is called a diazoamino compound I.



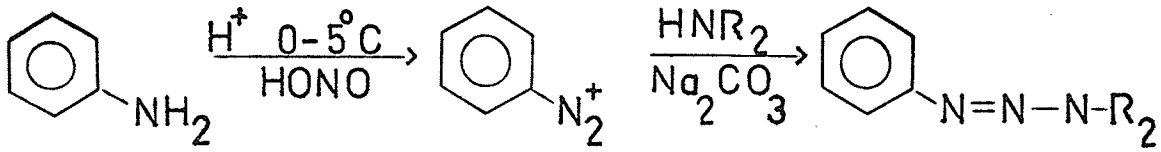
I.

If both of the N_3 hydrogens are replaced, we call the resulting triazene a diazoimino compound II.

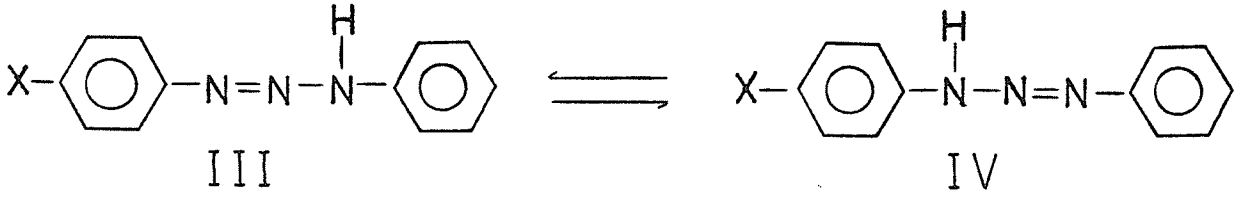


II.

The general method of preparation for triazenes (25) involves the nitrogen coupling of a diazotized amine to a free amine in a basic medium according to the following scheme:



For a long time, a great controversy existed with regard to the actual structure of diazoamino compounds since these can exist in two tautomeric forms.



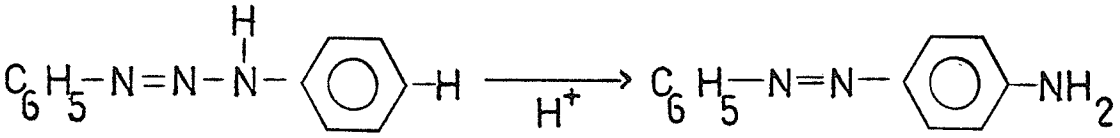
III IV

where X = any substituent used for labelling purposes.

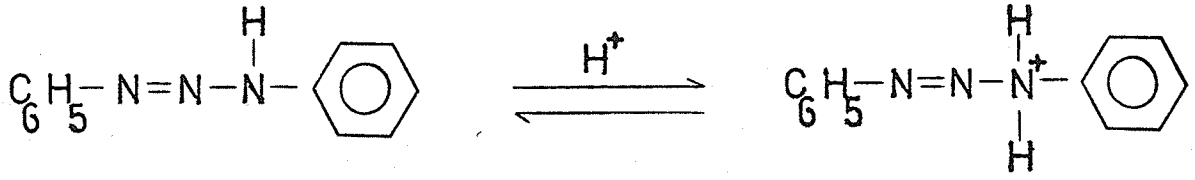
The question is, if one tries to make III or IV do we get a mixture of III and IV or do we get primarily one or the other but not both? Many attempts have been made to resolve this dilemma and the relevant work has been reviewed by Campbell and Day (8) and summarized by Zollinger(32). More recently, the question has been unequivocally settled by Gladkova (15,16) who concluded from his crystallographic structural studies that "the data attest to the equilibrium of two tautomeric forms in the given crystal." Of course, for diazoimino compounds such as II such prototropy is nonexistent due to the lack of a labile proton.

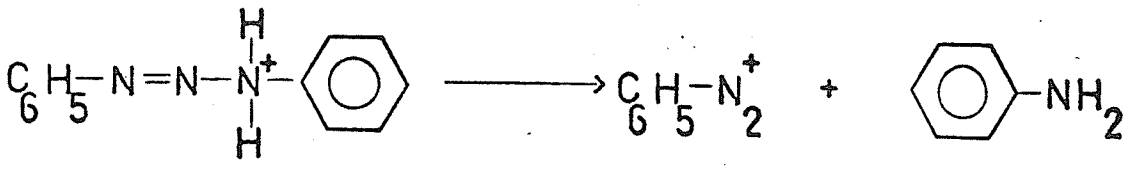
2. Known Modes of Decomposition

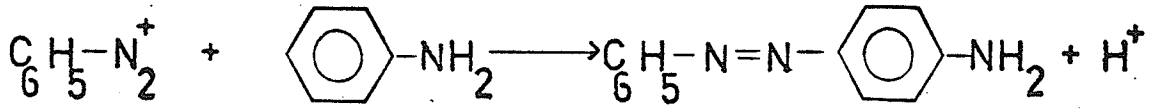
Decomposition of triazenes proceeds via different routes, depending on the reaction conditions. Triazenes have long been known to rearrange under acid conditions to form aminoazo dyes (32). The presence of the corresponding amine also enhances the reaction. The



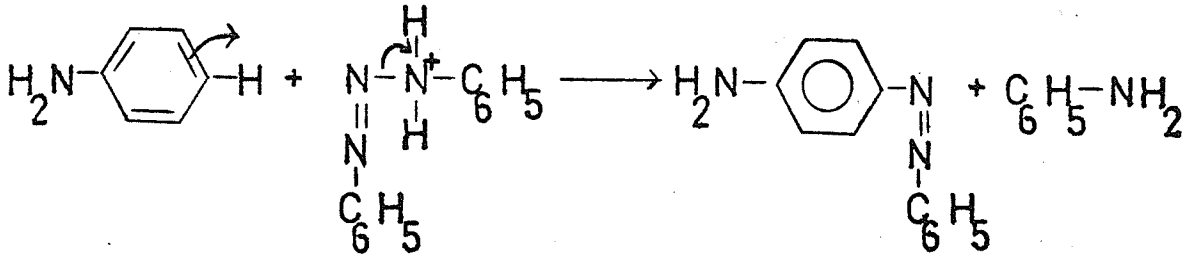
generally accepted mechanism for the reaction is the one first proposed by Friswell and Green (13,14).



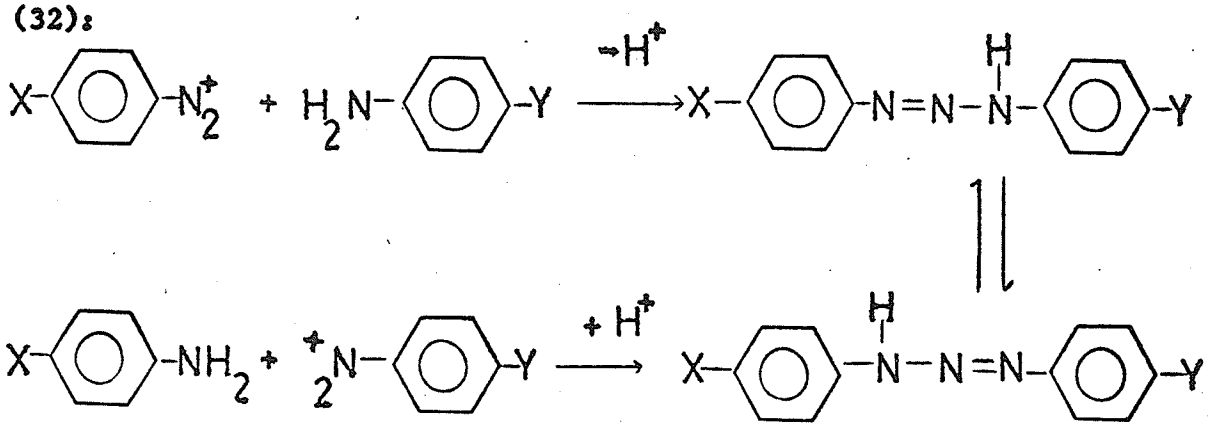




The major weakness of this mechanism is that it fails to explain why a poor yield of the azodye is formed when diazonium ions are added slowly to a solution of the amine under the same conditions as the preparative diazoamino rearrangement (60°-100° C) (32). This suggests that a mechanism of the type proposed by Goldschmidt(17) may be more realistic. Since aniline facilitates the rearrangement he proposed that a nucleophilic attack by aniline proceeds as follows:



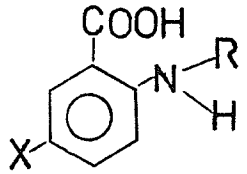
As a consequence of the prototropy which exists in diazoamino compounds, the latter may undergo a phenomenon known as diazo migration (32):



whereby a diazonium group is transferred from one aromatic moiety to

another via the intermediacy of a triazene.

Petitcolas and Thirot (24) studied the decomposition of triazenes of the type: $C_6H_5\text{-}N = N\text{-}N\begin{matrix}R\\R\end{matrix}$ (ie. diazoimino compounds) at room temperature. They followed the rate of decomposition as a function of pH in order to elucidate the mechanism of the reaction. The secondary amine chosen was the following:

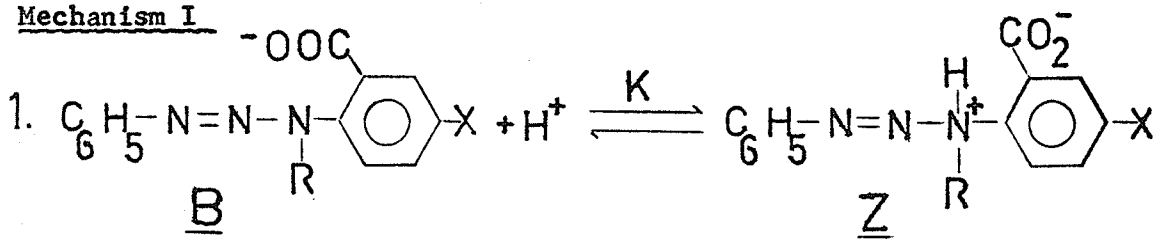


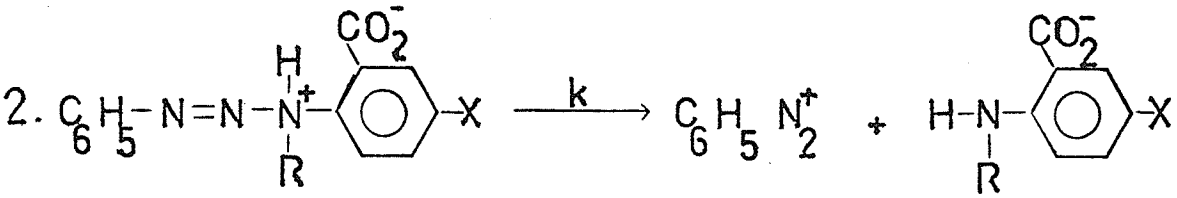
where R = alkyl or hydroxy alkyl

X = various functional groups.

They found that for a given triazene ($R = CH_2\text{-}CH_2\text{-}OH$) in the pH range six to ten at room temperature, the rate of decomposition increases as a function of the X substituent in the following order: $OCH_3 > NHCOCH_3 > H > Cl > Br > SO_3H > SO_2N(CH_3)_2 >$ 3,5 dichloro. In other words, electron releasing groups increase the rate of reaction. This data suggested to them a mechanism of the following type:

Mechanism I





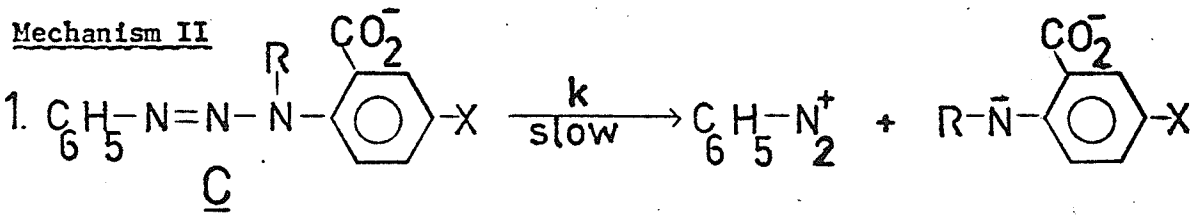
This substituent effect has been interpreted to mean that as the basicity of N_3 is increased by electron releasing substituents, K and [Z] increase and hence the overall rate of decomposition increases since

the rate = k [Z].

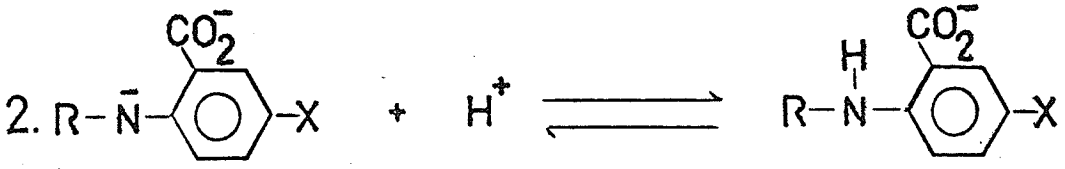
The following triazene $C_6H_5-N=N-\underset{\displaystyle CH_3}{\underset{|}{N}}-CH_2-COOH$ was decomposed and a faster rate of decomposition was predicted for it since N_3 was now more basic than in A. The rate was observed not to be faster, and on this basis the authors reject the above mechanism. However, we think that the latter may not be sufficient cause to reject the above mechanism since the difference in rates might be due to the difference in nucleophilicity of the aliphatic amine relative to the aromatic amine in the rate determining step 2.

Another mechanism which has tentatively been proposed in the same paper is the following:

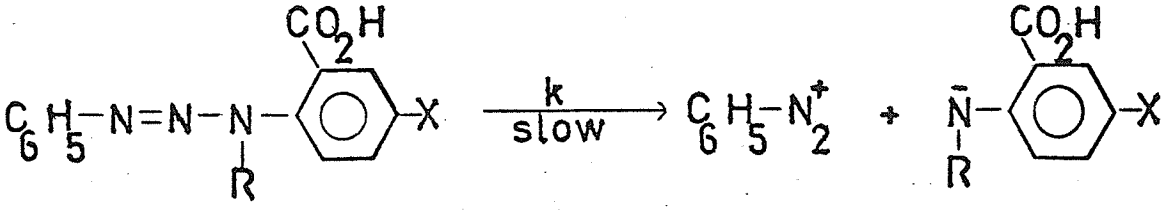
Mechanism II

1. 

C

2. 

The above mechanism also has to be rejected since a plot of the observed rate constant k versus $[H^+]$ gives a slope of +1. If the following modification is made to the above mechanism, then the pH effect can be rationalized.

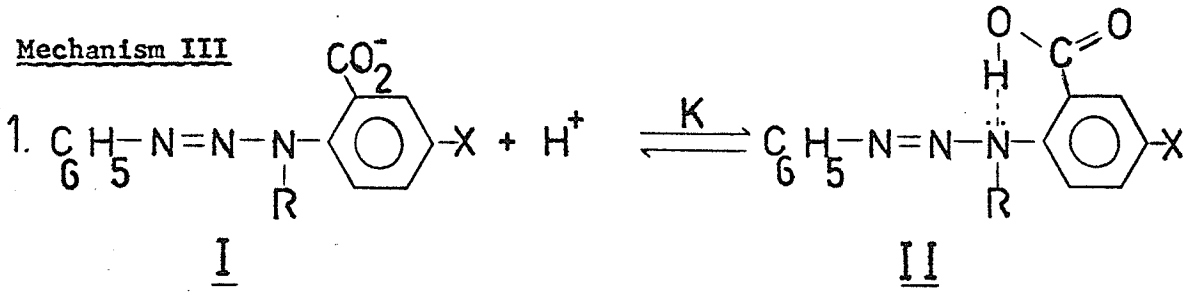


D

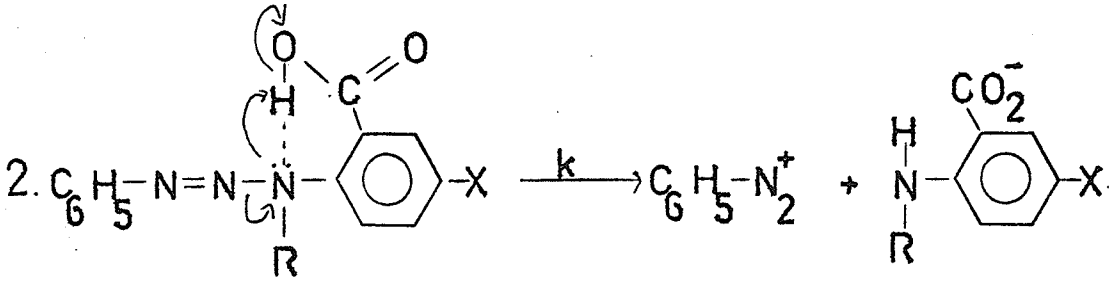
As the hydrogen ion concentration increases, the concentration of D will increase relative to C and hence the overall rate of decomposition will increase since rate = k [D]. This mechanism must also be rejected, however, since electron releasing substituents at X would be expected to hinder the rate determining step by increasing the nucleophilicity of N_3 which is contrary to the observed results.

In order to account for the pH effects and the observed substituent effects, Petitcolas and Thirot develop a mechanism which assigns a special role to the ortho carboxyl group.

Mechanism III



I II



The rate expression is now

$$\text{rate} = k\,[II] = k\,K\,[I][H^+]$$

For a given hydrogen ion concentration, the effect of electron releasing substituents X is to decrease the acidity of the carboxyl group and therefore K will increase and the observed rate should increase which is in accordance with the experimental results.

If $[H^+]$ increases, II will increase, therefore the overall rate

should increase which is also in accordance with the observed experimental results.

In our opinion, these authors' results do not allow them to distinguish between mechanisms I and III since both the substituent effects and the pH effects predict the same results for both the proposed mechanisms I and III. Therefore, the "special role" of the ortho carboxyl group has not been established by these studies.

Andakushkin (2) studied the thermal decomposition of triazenes of the type $R\text{-}N = N\text{-}\overset{H}{\underset{|}{N}}\text{-}C_6H_5$ in buffered aqueous systems and found that the decomposition rates are fastest at pH = 1, while at pH's greater than ten, the triazenes decomposed only very slowly. He also studied the decompositions in wet organic solvents at 20° - 40°C. Although he observed no decomposition in dry organic solvents at 40°C, he found that the rate of decomposition gradually increases with increasing water concentration. From his results, Andakushkin concluded that the reaction proceeds as follows in wet organic solvents:

1. $Ar\text{-}\overset{H}{\underset{|}{N}}\text{-}N = N\text{-}R + HOH \longrightarrow Ar\text{-}NH_2 + R\text{-}N = N\text{-}OH$

2. $R\text{-}N = N\text{-}OH \longrightarrow R\cdot + \cdot OH + N_2$

3. $R\cdot + \cdot OH \longrightarrow R\text{-}OH$

He later found (3) that the decomposition was catalysed by $FeSO_4$ and Na_2SO_4 and that these also initiate the decomposition of the diazohydroxide in the following fashion:

$$R\text{-}N = N\text{-}OH + Fe^{++} \longrightarrow R\cdot + N_2 + OH^- + Fe^{+++}$$

Alferova (1) also studied the decomposition of aliphatic-aromatic triazenes in aqueous alcoholic mixtures in the presence of acetic acid

from 50° - 90°C and found that the decomposition proceeds according to an ionic mechanism with the formation of aniline, N_2, alcohol, or the corresponding ester and unsaturated hydrocarbon:

1. $C_6H_5-\overset{H}{\underset{|}{N}}-N = N-R + R'-\overset{O}{\overset{||}{C}}-OH \longrightarrow C_6H_5-NH_2 + R-N = N-O-\overset{O}{\overset{||}{C}}-R'$

2. $R-N = N-O-\overset{O}{\overset{||}{C}}-R' \longrightarrow R-\overset{+}{N} \equiv N + R'-\overset{O}{\overset{||}{C}}-O^-$

3. $R-N_2^+ \longrightarrow R^+ + N_2$

He also reported that at elevated temperatures, the reaction appears to proceed both by the ionic and radical mechanisms in neutral solution.

Hardie and Thompson (18) have studied the thermal decomposition of triazenes in non-aqueous solvents. They found that diaryltriazenes decompose homolytically at 150° - 160°C in aromatic solvents to yield phenyl and anilino radicals in the following fashion:

1. $C_6H_5-N = N-\overset{H}{\underset{|}{N}}-C_6H_5 \longrightarrow N_2 + C_6H_5\cdot + C_6H_5\dot{N}H$

2. $C_6H_5\cdot + C_6H_5NH\cdot \longrightarrow C_6H_5-\underset{H}{\underset{|}{N}}-C_6H_5$

3. $C_6H_5\cdot + C_6H_6 \longrightarrow C_6H_5-C_6H_5 + H\cdot$

4. $C_6H_5-\dot{N}-H\cdot + H \longrightarrow C_6H_5-NH_2$

Dolgoplosk (11,12) found that in other non-aqueous solvents such as hydrocarbons, a similar mechanism held:

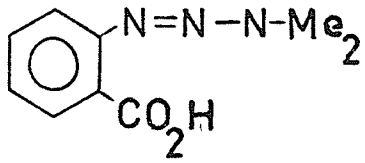
1. $R-N = N-\overset{H}{\underset{|}{N}}-\phi \longrightarrow R\cdot + N_2 + \phi-\dot{N}-H$

2. $2R\cdot \longrightarrow R-R$

3. $R\cdot + \phi-\dot{N}-H \longrightarrow \phi-\overset{R}{\underset{|}{N}}-H$

Recently, Nakayama, Simamura and Yoshida (23) have studied the thermal decomposition of 1-(2-carboxyphenyl)-triazenes in non-aqueous

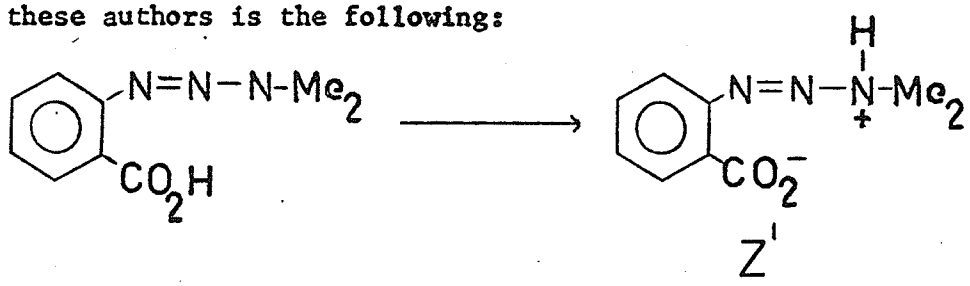
solvents. They heated 1-(2-carboxyphenyl)-3,3-dimethyltriazene (hereafter to be called A') in refluxing acetic acid for thirty minutes;



A'

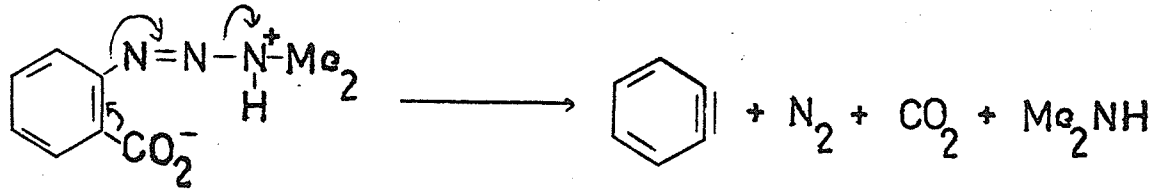
and found a 70% yield of salicylic acid, an 85% yield of N,N-dimethylacetamide and a 12% yield of phenyl acetate. The formation of phenyl acetate lead them to suspect that benzyne might be generated from the decomposition of the triazene since phenyl acetate corresponds to the addition of acetic acid to benzyne. To test this hypothesis, they heated A' in chlorobenzene in the presence of 2,3,4,5-tetraphenylcyclopentadienone and got a yield of 80% (based on A') of the corresponding benzyne adduct 1,2,3,4-tetraphenylnaphthalene. The mechanism proposed by these authors is the following:

1.



Z'

2.

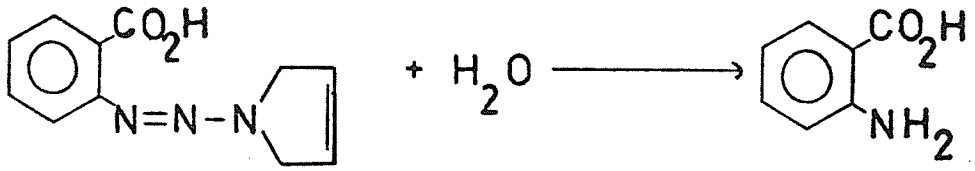


The test described above was repeated for the methyl ester of A' but no benzyne adduct could be isolated. This, the authors claim provides strong evidence for the formation of the inner salt Z' in the generation of benzyne from 1-(2-carboxyphenyl)-triazenes.

3. New Mode of Decomposition

Dayal (10) reported a decomposition product for A which could

not be accounted for by any of the previously reported modes. He found that decomposition of A in the presence of water gave a product identified as anthranilic acid.



He also followed the rates of decomposition of A in several buffer solutions at 40°C by following the change in absorbance of A at 270 nm . From the u.v. spectra of the product he concluded that the only product of decomposition of A was anthranilic acid. A summary of his results appears in the form of a pH rate profile in Fig. 1. It is seen that the rate of decomposition increases in the pH region 1 - 2 but levels out rather quickly after pH = 3. He also found that in 1 N. NaOH, A is stable and does not decompose. This implies that the pH profile must return to the abscissa at some pH greater than seven. On the basis of his experimental results, Dayal suggested the following tentative mechanism Scheme I.

Since the most basic nitrogen in A is probably the pyrroline nitrogen, it was postulated that in acidic solutions, A is protonated on this site to give HA^+. Because decomposition was found to be very slow under moderately strong acid or basic conditions, Dayal proposed that only neutral A decomposes to anthranilic acid. He proposed that A decomposes by way of the zwitterion Z and that the o-carboxyl group provides the necessary proton to convert A to the zwitterion. The zwitterion expected to be present in the largest concentration is the following:

FIGURE 1

Dayal's pH Rate Profile for the Decomposition of A

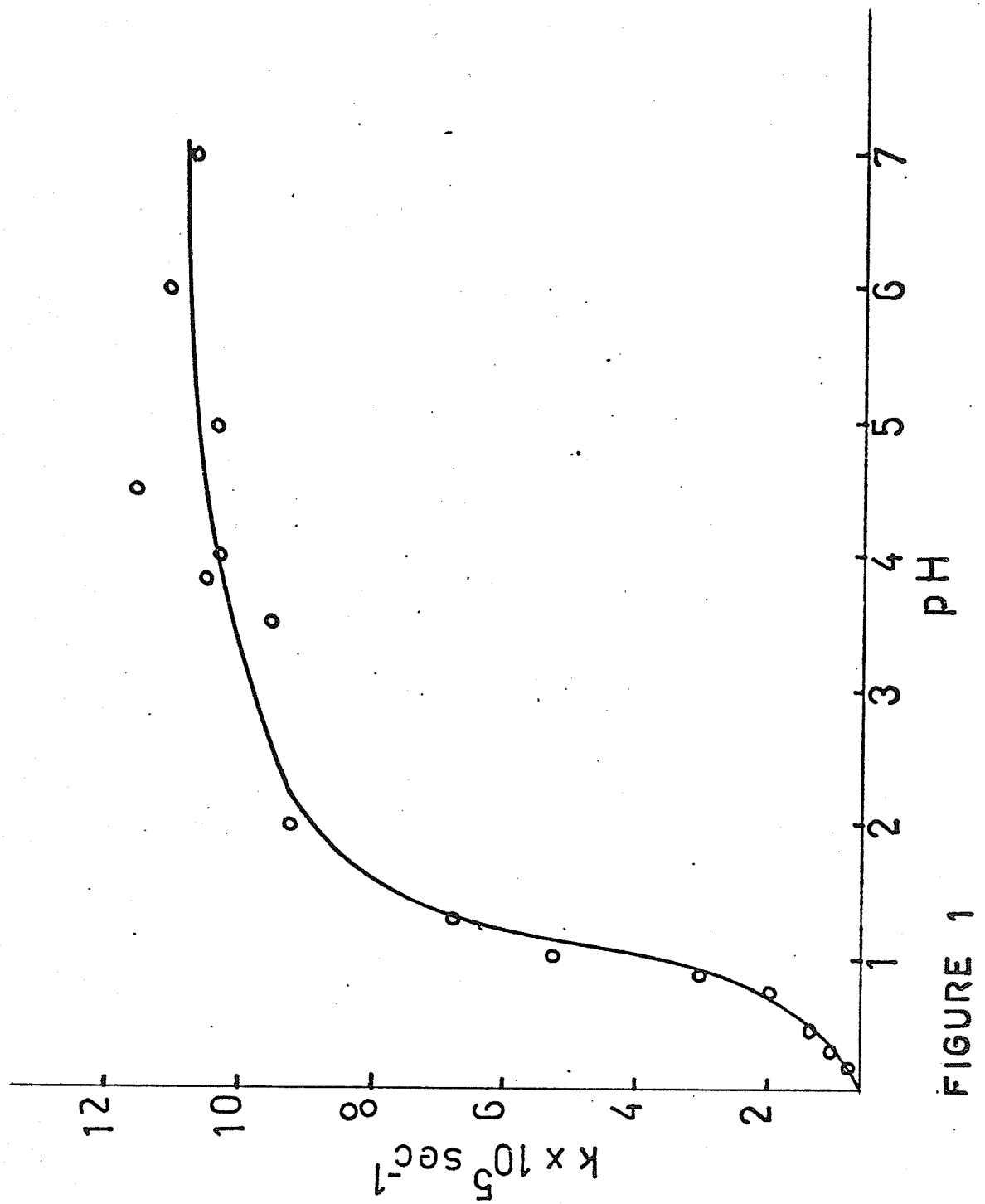
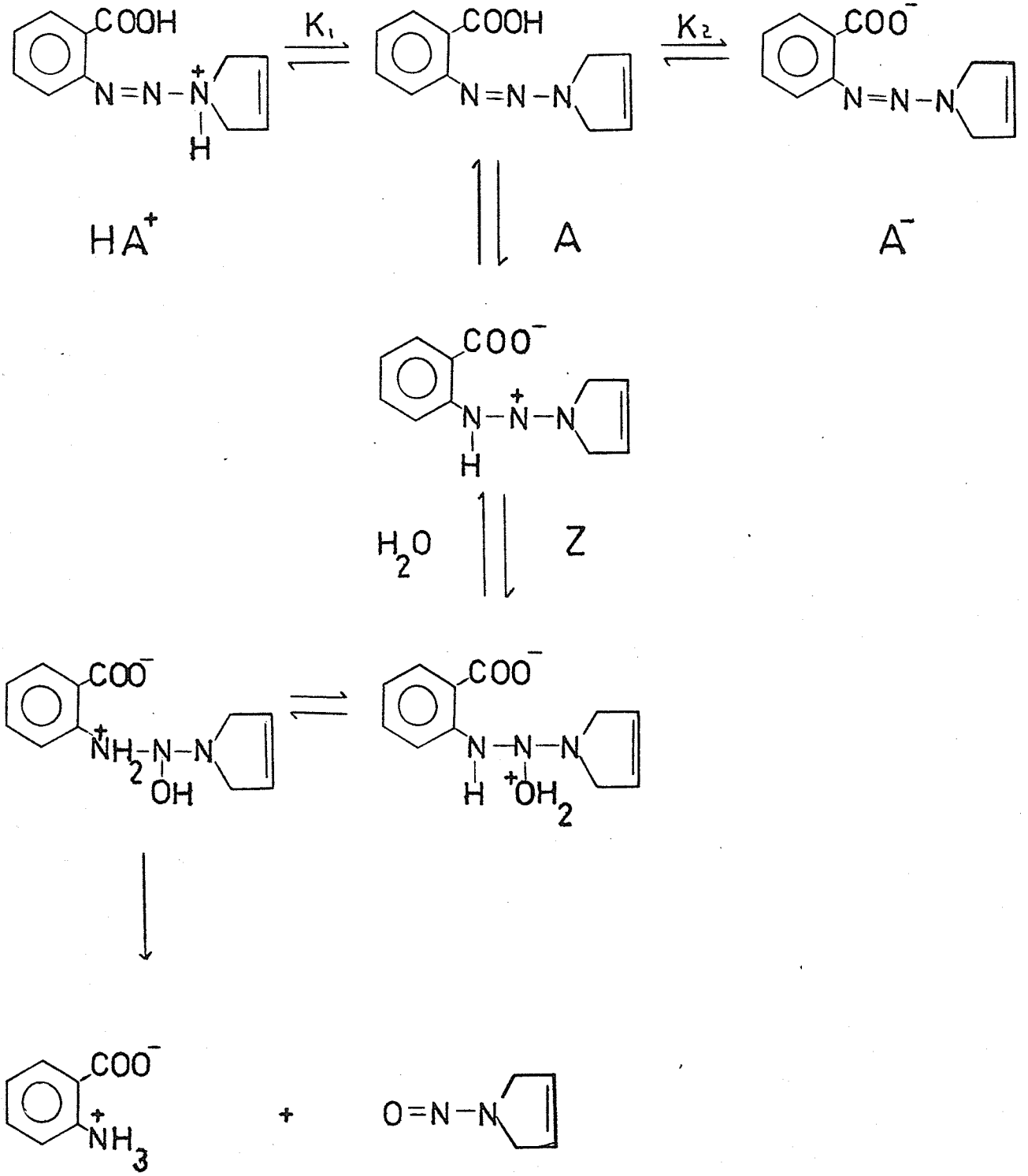
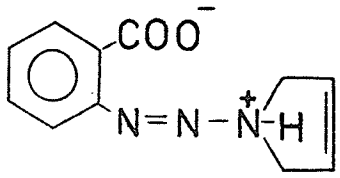


FIGURE 1

SCHEME I

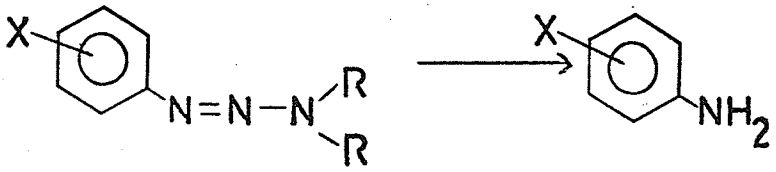

COOH
N=N-N
H
K1
COOH
N=N-N
K2
COO⁻
N=N-N
HA⁺
A
A⁻
COO⁻
N-N-N
H
H2O
Z
COO⁻
NH2-N-N
OH
COO⁻
N-N-N
H
OH2
COO⁻
NH3
+
O=N-N



Since the latter zwitterion could hardly lead to the formation of anthranilic acid, it was proposed that the zwitterion Z, although present in lower concentrations, is the one leading to the formation of anthranilic acid. No N-nitroso-3-pyrroline was isolated; in fact, no product originating from the pyrroline was recovered. It was assumed that the pyrroline residues were lost through oxidation and/or polymerization. Dayal also attempted to determine the pK's of A, but decomposition in aqueous solutions was significant even at 20°C and therefore further attempts were abandoned.

III. OBJECT OF THIS WORK

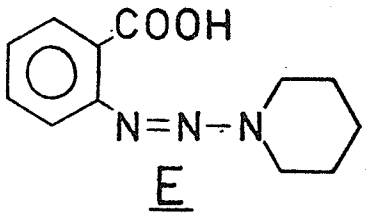
From the previous discussion it is obvious that triazenes may decompose via different modes depending on the structure of the respective triazenes, the solvent, the temperature and finally the pH of the solution. However, none of these known modes of decomposition can account for Dayal's reported formation of aromatic amine from a diazoimino compound in aqueous solution.



The object of this investigation was to find out what reaction conditions favour the formation of aromatic amine. Having accomplished this, we also wanted to study the kinetics of the reaction, disappearance of triazene and appearance of aromatic amine in order to elucidate the mechanism for this reaction path way. We soon realized that mass balance based on the aromatic moiety of the molecule was not achieved during the course of the decomposition product analysis. In other words, the sum of the aromatics found did not add up to the expected amount based on the original triazene concentration. As a result of this discrepancy we decided to study how different substituents would affect the yield of aromatic amine.

IV. RESULTS

1. 1-(2-carboxyphenyl)-3-piperidinotriazene (E)



E

Compound E was synthesized by coupling diazotized anthranilic acid with piperidine in a basic medium as recommended by Rondesvedt and Davis (25) for the synthesis of triazenes. Piperidine was chosen as the secondary amine because Dayal (10) had suspected that N-nitrosopyrroline was readily subject to oxidation and polymerization reactions. However, works done in this laboratory by Dr. G.R. Taylor (30) showed that N-nitrosopiperidine was a stable compound under the conditions of the decomposition of E. He also showed that N-nitrosopiperidine was not a final product in the decomposition of E since the u.v. spectrum of the decomposition products showed no similarities to the u.v. spectrum of N-nitrosopiperidine.

The investigation began by trying to determine the rates of decomposition of E. The usual way of doing this is to follow the disappearance of reactant or appearance of product as a function of time using some suitable analytical method to monitor the respective concentrations. One of the simplest ways of doing this is to follow changes in absorbance of a species in the u.v. spectrum as a function of time. The main requirement of the method is that product and reactant must show absorbance characteristics at sufficiently different wavelengths to avoid mutual interference.

Compound E was decomposed at room temperature in various buffer

solutions ranging from pH 1.2 to 8 and its u.v. spectrum scanned at various time intervals for each pH. An aliquot of a stock solution of E (in 0.1 N NaOH) was added to a non-thermostated u.v. cell already containing a known volume of the buffer, and the spectrum was scanned immediately after thorough mixing of the solution. Some of these spectra are shown in Fig.'s 2,3,4 for the pH's 2.8, 7 and 8 respectively. It was observed qualitatively by comparing the appropriate half lives of E at the various pH's that the rate of decomposition follows a pH rate profile similar to the one given by Dayal (10) Fig. 1. However, at pH's greater than 6 the rate of decomposition begins to decrease.

In Fig. 2, the isosbestic points at 272 and 258 nm strongly suggest that E is decomposing primarily to one product, say E'. However, the isosbestic points at 307 and 289 nm suggest that E' is undergoing further decomposition to some other product, let us call it E''. All pH's up to and including 6 show this same isosbestic point pattern, but at pH 7 Fig. 3, the two higher wavelength isosbestic points disappear and at pH 8, Fig. 4, all the isosbestic points have disappeared. Clearly, the decomposition appears to be getting more complicated as the pH of the buffer increases beyond 6.

Dayal (10) concluded from the u.v. spectrum of the product of decomposition of A (Page 2 this thesis) that the only aromatic product formed was anthranilic acid. Fig. 5 shows the pH dependence of anthranilic acid in the u.v. spectrum. As the pH increases, the absorbance increases in the region of 312 nm and decreases in the region of 272 nm. However, the spectrum of E'' in Fig. 2 shows that its absorption maximum occurs at about 296 nm. Therefore, E'' cannot be anthranilic acid. Fig. 6 shows a u.v. spectrum of salicylic acid as a function of pH. The absorbance maximum at 296 nm suggests that E'' may be salicylic acid. Further evidence for the presence of salicylic acid was

FIGURE 2

Decomposition of E at pH 2.8 as a Function of Time

NOTE: The numbering proceeds from left to right beginning at the left margin on the base line of the sprectrum.

1. .5 minutes
2. 1.5 minutes
3. 3 minutes
4. 4.5 minutes
5. 6 minutes
6. 7 minutes
7. 10 minutes
8. 2 hours
9. 4 hours
10. 24 hours

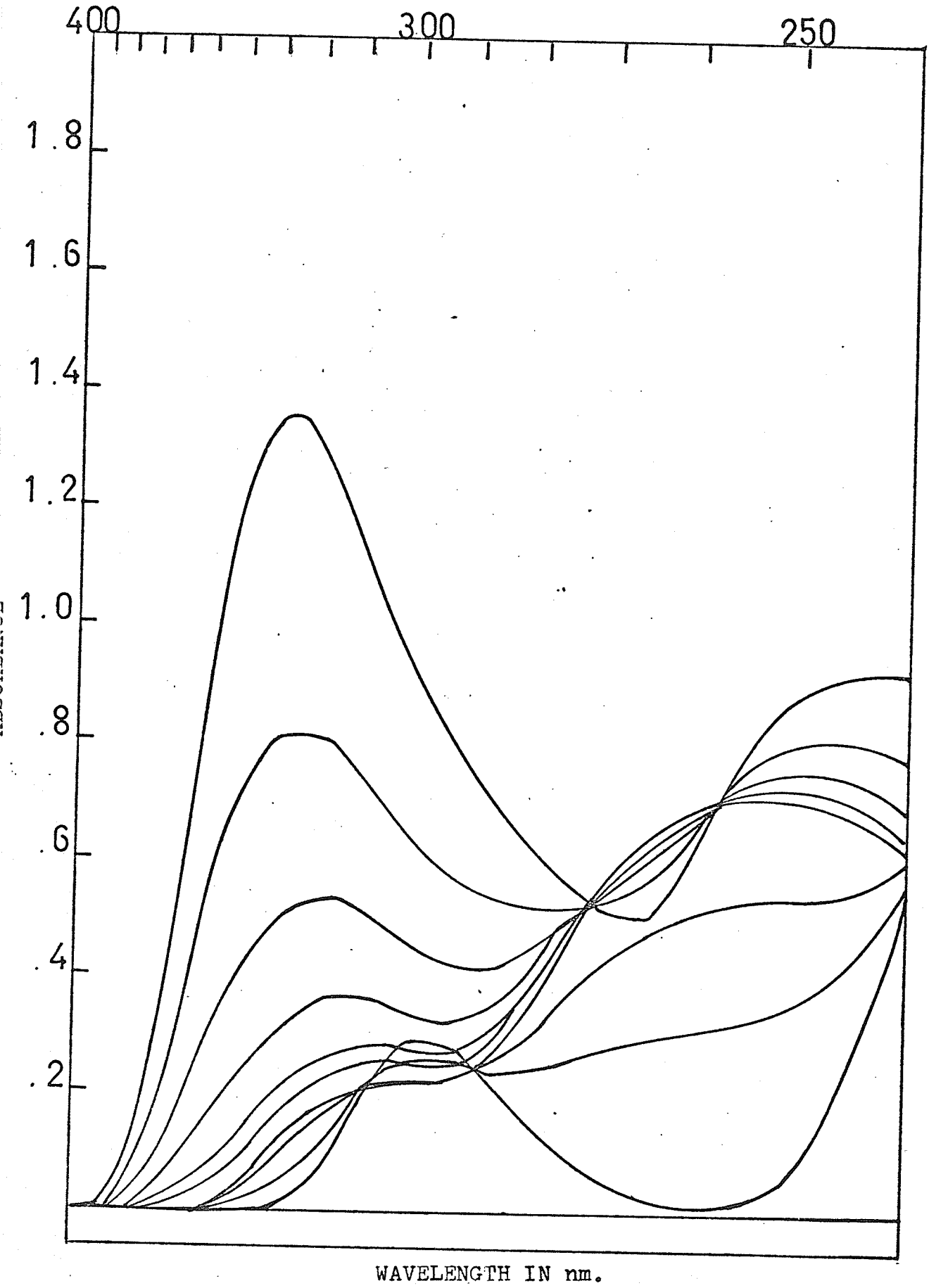


FIGURE 2

FIGURE 3

Decomposition of E at pH 7 as a Function of Time

1. 15 seconds
2. 5 minutes
3. 15 minutes
4. 45 minutes
5. 2.0 hours
6. 2.5 hours
7. 5.0 hours
8. 48 hours

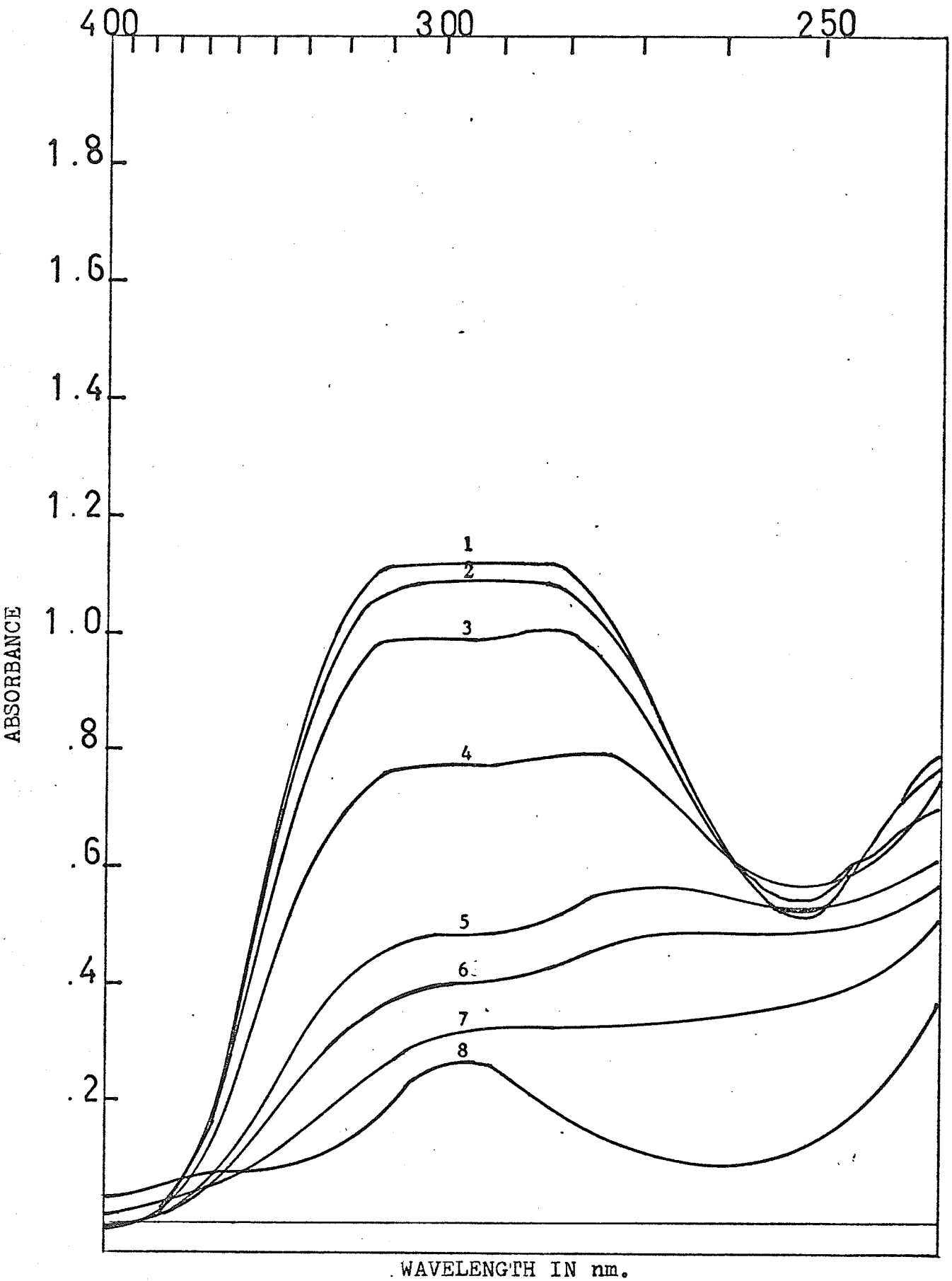

400
300
250
1.8
1.6
1.4
1.2
1.0
.8
.6
.4
.2
ABSORBANCE
1
2
3
4
5
6
7
8
WAVELENGTH IN nm.

FIGURE 3

FIGURE 4

Decomposition of E at pH 8 as a Function of Time

1. 20 seconds
2. 30 minutes
3. 90 minutes
4. 22 hours
5. 31 hours

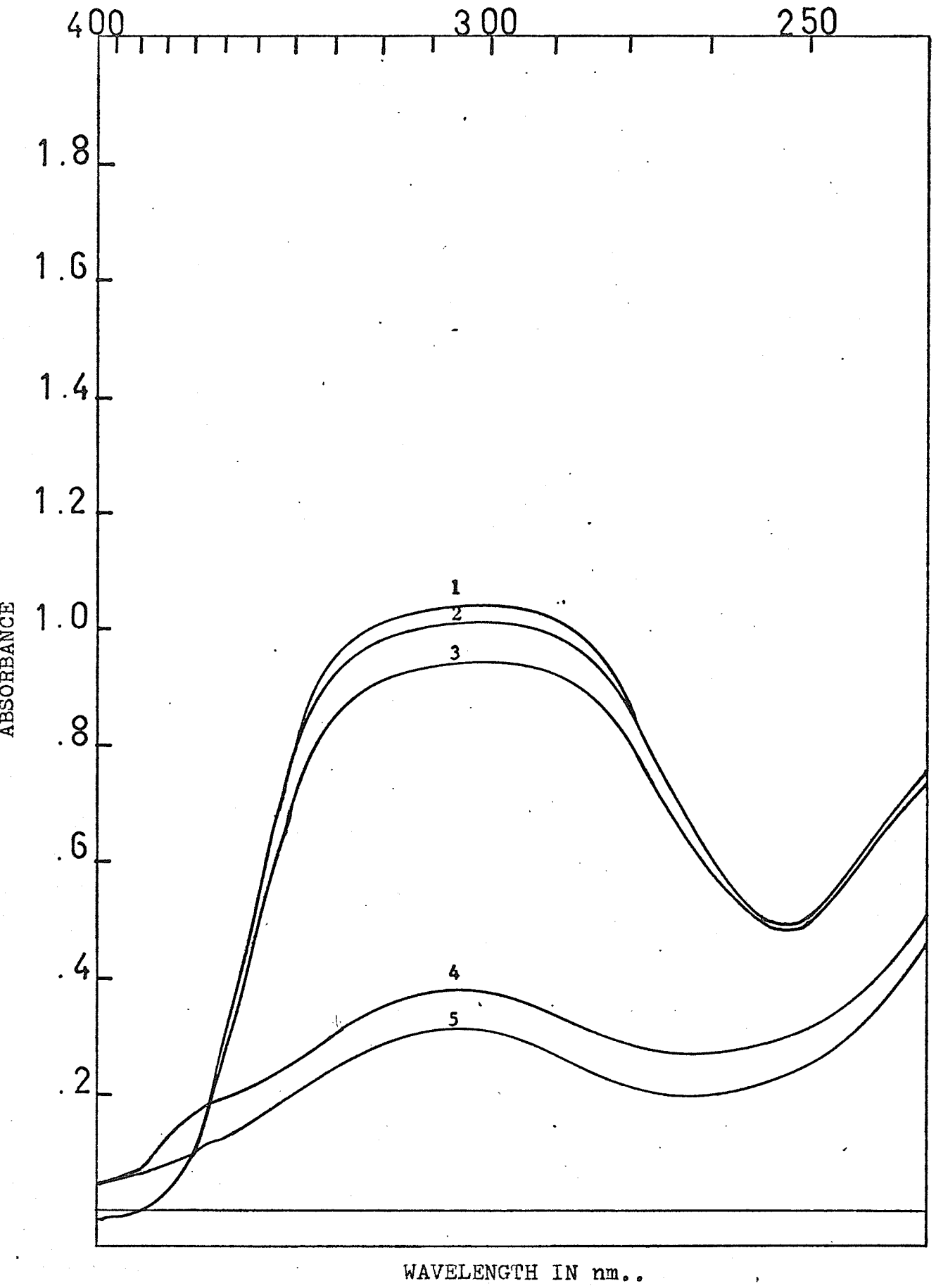

400
300
250
1.8
1.6
1.4
1.2
1.0
.8
.6
.4
.2
ABSORBANCE
1
2
3
4
5
WAVELENGTH IN nm..

FIGURE 4

FIGURE 5

Spectrum Showing pH Dependence of Anthranilic Acid

1. pH 6
2. pH 4
3. pH 2
4. pH 1
5. pH 0

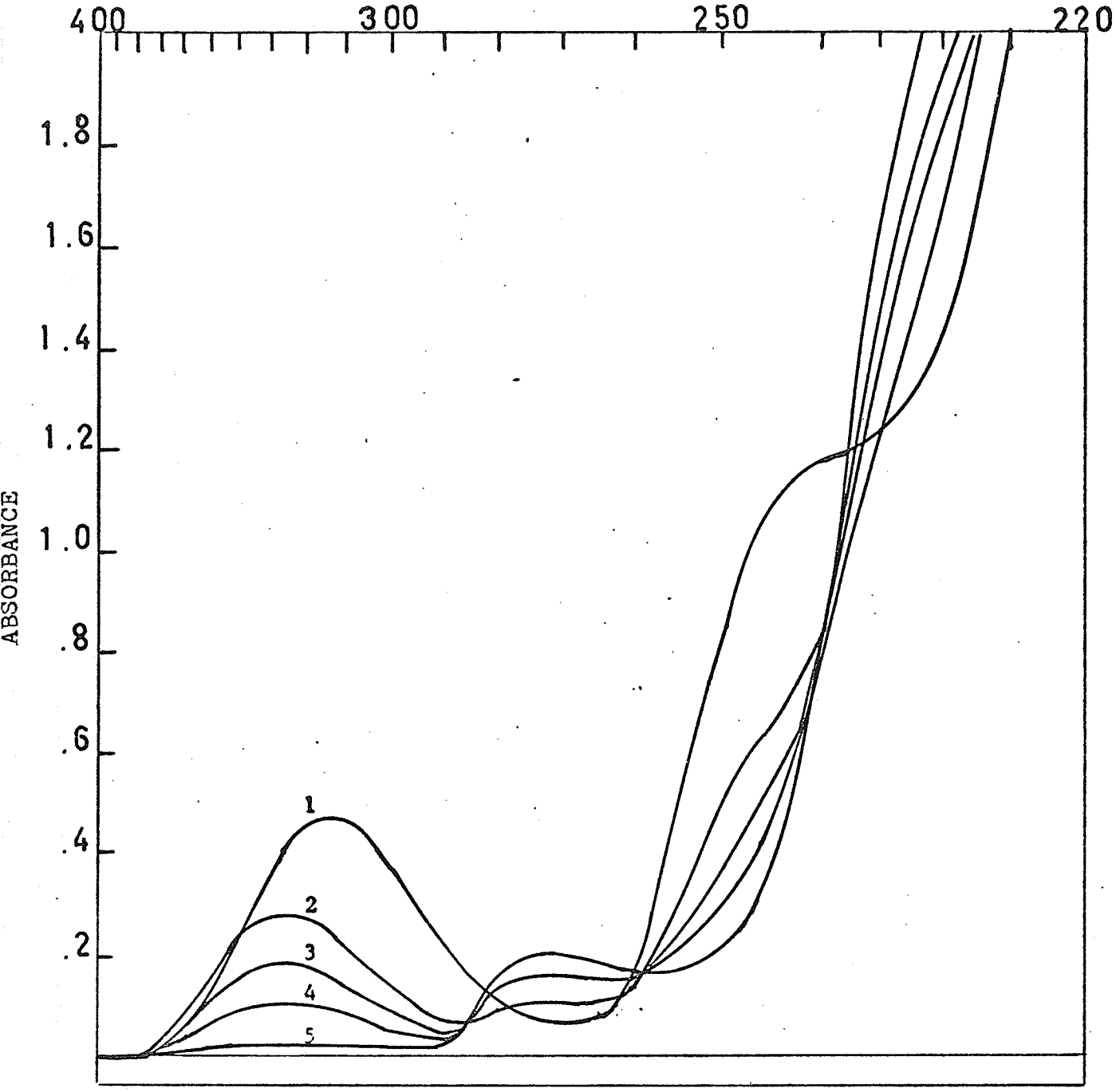

400
300
250
220
1.8
1.6
1.4
1.2
1.0
.8
.6
.4
.2
ABSORBANCE
1
2
3
4
5
WAVELENGTH IN nm.

FIGURE 5

FIGURE 6

Spectrum Showing pH Dependence of Salicylic Acid

1. pH 8

2. pH 2

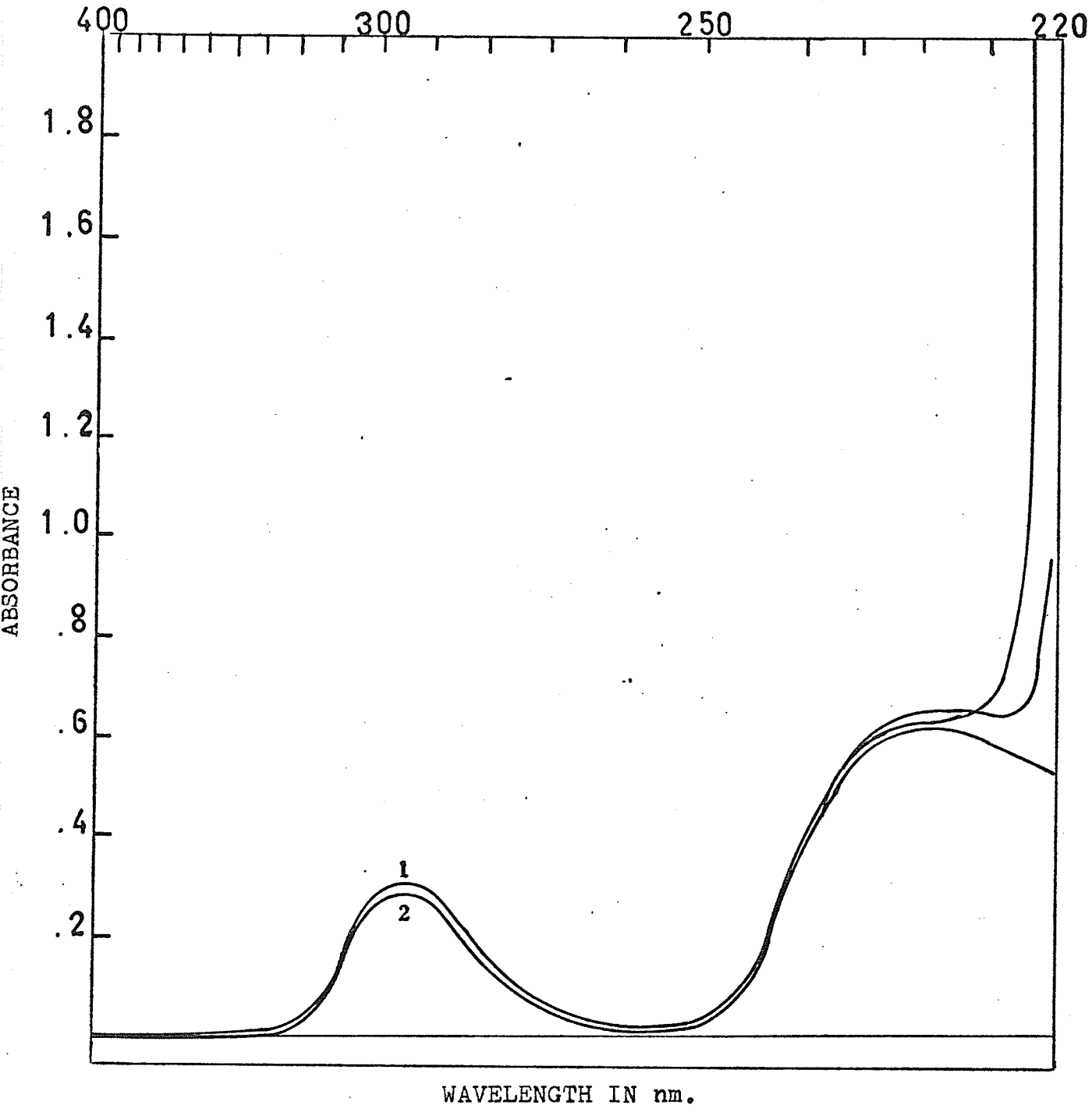

400
300
250
220
1.8
1.6
1.4
1.2
1.0
.8
.6
.4
.2
ABSORBANCE
1
2
WAVELENGTH IN nm.

FIGURE 6

provided by a colorimetric method to be described later.

The formation of salicylic acid is perhaps not too surprising since it is well known that triazenes may decompose under acid conditions to give diazonium ion and secondary amine (32,24), i.e. the reversal of the formation of the triazene. The diazonium ion can subsequently react with water to give substituted phenol and nitrogen in the following way:

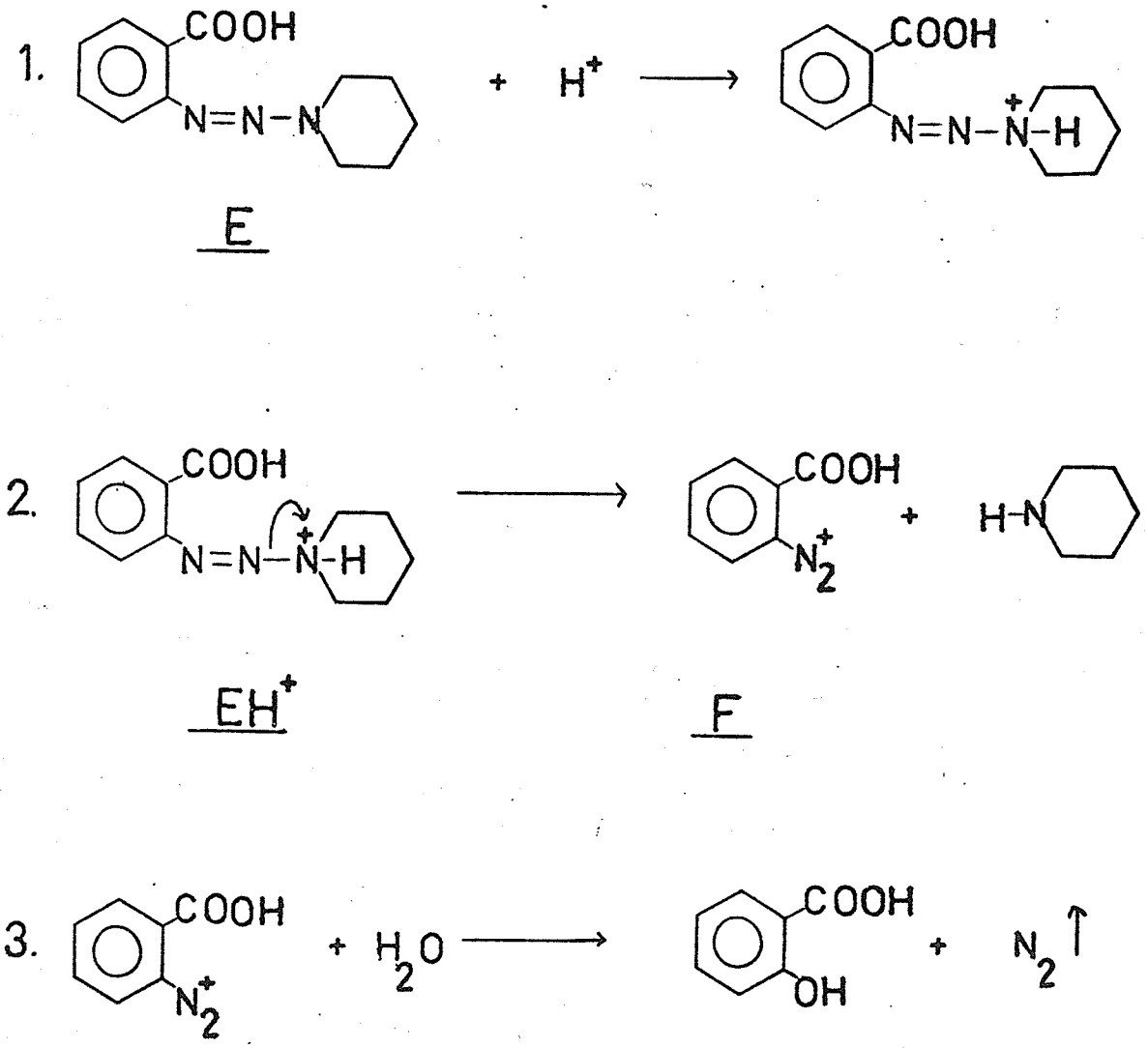


Fig. 7 shows spectra of 2-carboxybenzenediazonium ion F decomposing in a u.v. cell as a function of time. The initial spectrum has an

FIGURE 7

u.v. Spectrum of 2-carboxybenzenediazonium ion as a Function of Time

1. 1 minute
2. 2 minutes
3. 3 minutes
4. 4 minutes
5. 60 minutes

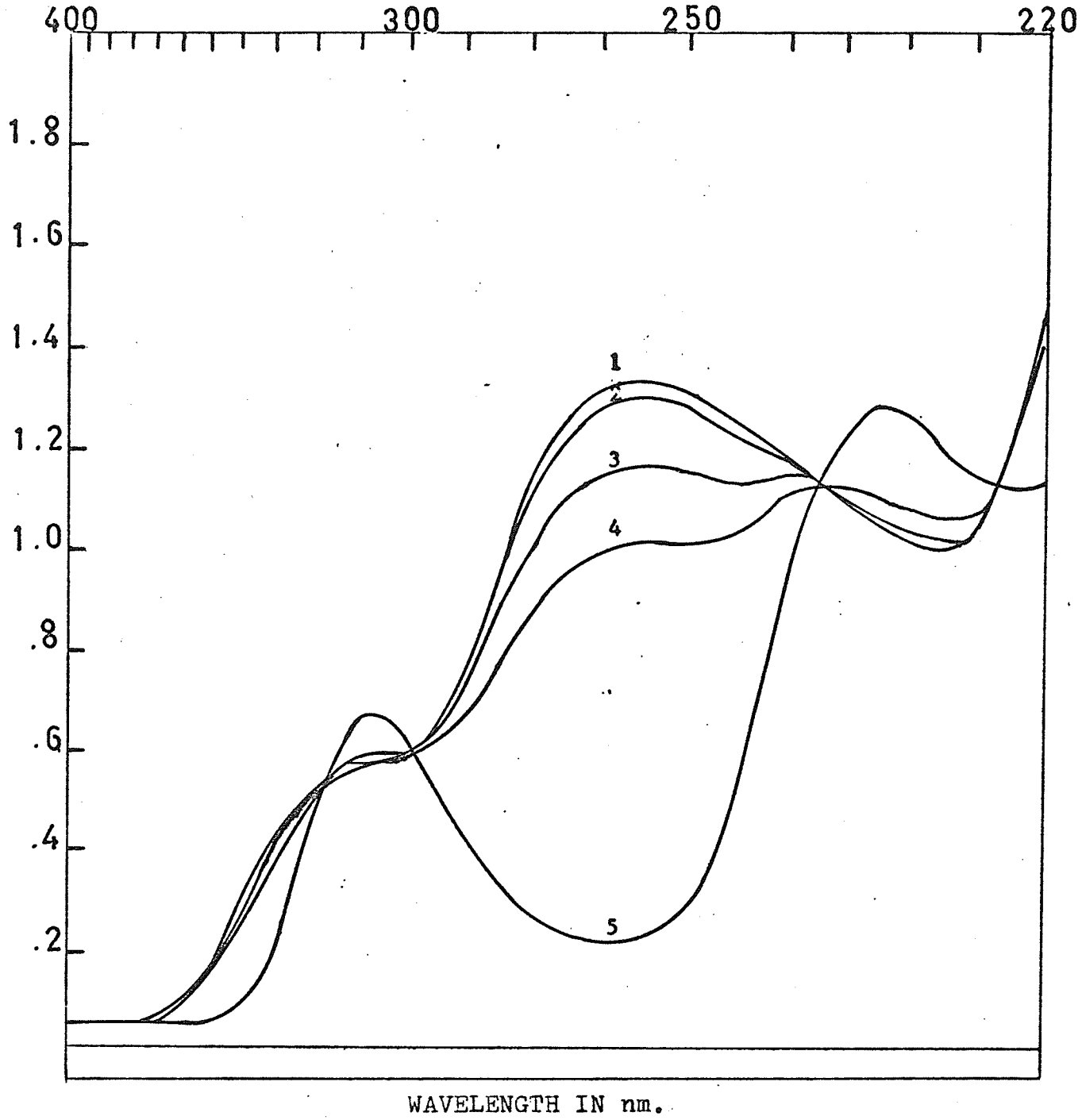

400
300
250
220
1.8
1.6
1.4
1.2
1.0
.8
.6
.4
.2
ABSORBANCE
1
2
3
4
5
WAVELENGTH IN nm.

FIGURE 7

absorption maximum at 255 nm. A similar absorption pattern can be seen in the spectrum of E decomposing in Fig. 2. Note that the spectra of F also show isosbestic points at 307 and 289 nm. It would seen reasonable, then, to interpret Fig. 2 as follows: under acid conditions, EH^+ is decomposing to diazonium ion F (isosbestic points at 272 and 258 nm); then F reacts with water to give salicylic acid E'' (isosbestic points at 307 and 289 nm).

It is obvious from the spectra in Fig.'s 2 to 4 that the rate of decomposition of E would only be studied by u.v. under acid conditions, since at higher pH's the absorption of products interfere (see Fig. 4). However, the concentrations of the products can be followed by converting them to other species having absorption maxima which do not conflict with that of the reactant.

To do this, advantage was taken of the fact that many aromatic phenols, including salicylic acid, will react with ferric ion to form a coloured complex in acid solution; see Fig. 8 for salicylic acid plus ferric ion spectrum. Fig. 8 shows that the abosrption maximum is at 525 nm and that the absorbance is highly pH dependent. It also shows the time-dependent stability of the complex, since each spectrum was repeatedly scanned from ten minutes after mixing up to two hours after mixing with no visible change in absorbance over the time period. The only limitations encountered with this colorimetric method is the rigid pH control required and the interference caused by phosphate buffers. Phosphate buffers covering the pH range 6 to 9 could not be used because of a precipitate which is formed in the presence of ferric ion. This problem was easily eliminated by using other buffers such as sodium hydrogen succinate plus sodium succinate in the pH range 5.8 to 6.2 and boric acid plus borax in the pH range 6.7 to 9.2.

FIGURE 8

Visible Spectrum of Salicylic Acid Plus Ferric Solution as a Function of pH

1. pH 1.74
2. pH 1.31

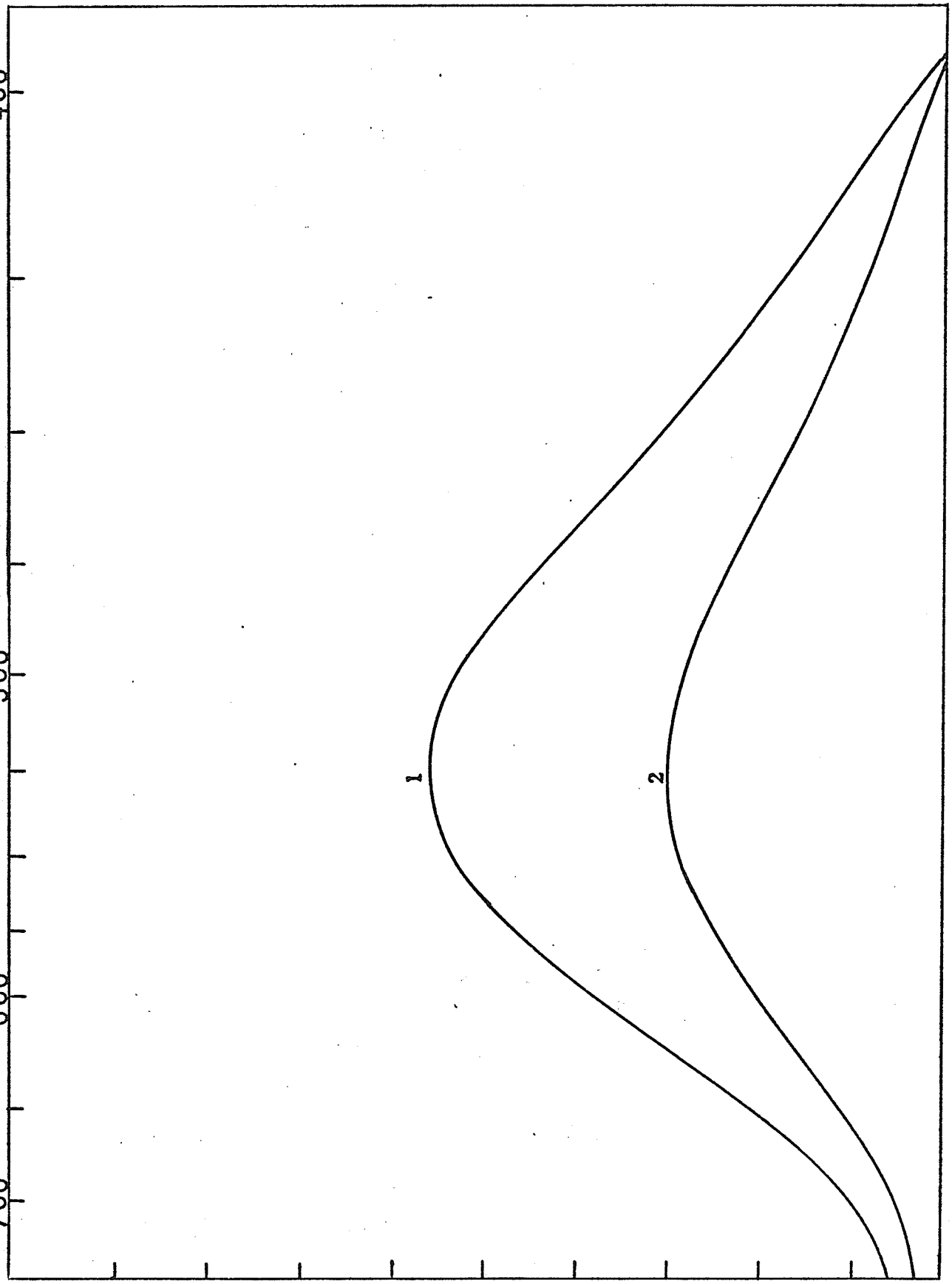

ABSORBANCE
1.8
1.6
1.4
1.2
1.0
.8
.6
.4
.2
700
600
500
400
1
2
WAVELENGTH IN nm.

FIGURE 8

The pH control problem was solved by calibrating for salicylic acid prior to each decomposition of E. Reference salicylic acid mixtures were buffered to exactly the same pH as that used in the decomposition of E so that an aliquot of salicylic acid solution plus an aliquot of ferric ion solution would give the same resulting pH as an aliquot of solution E plus an identical aliquot of ferric ion solution.

The concentration of anthranilic acid was followed using a colorimetric method previously reported by Kupfer and Atkinson (20). The method is based on the formation of a Schiff base between a primary amine such as anthranilic acid and p-dimethylaminobenzaldehyde (PDAB).

Fig. 9 shows a spectrum of the resulting Schiff base having a maximum abosrbance at 450 nm. The Schiff base was shown to be stable for at least eight hours after mixing the primary amine and the PDAB solution.

Compound E was decomposed at 50°C in an oil bath in buffers ranging from pH 5 to 8 and the product concentrations were monitored using the above described colorimetric procedures. Table 1 shows a

Table 1

pH	5.14	6.04	7.96
% yield anthranilic acid	0.0	1.2	20.0
% yield salicylic acid	99.0	96.5	37.5
Total mass balance	99.0	97.7	57.5

summary of the resulting product distributions at 50°C. As pH increases, one observes an increase in the yield of anthranilic acid, a decrease

FIGURE 9

Spectrum of the Schiff Base Formed From

Anthranilic Acid plus PDAB

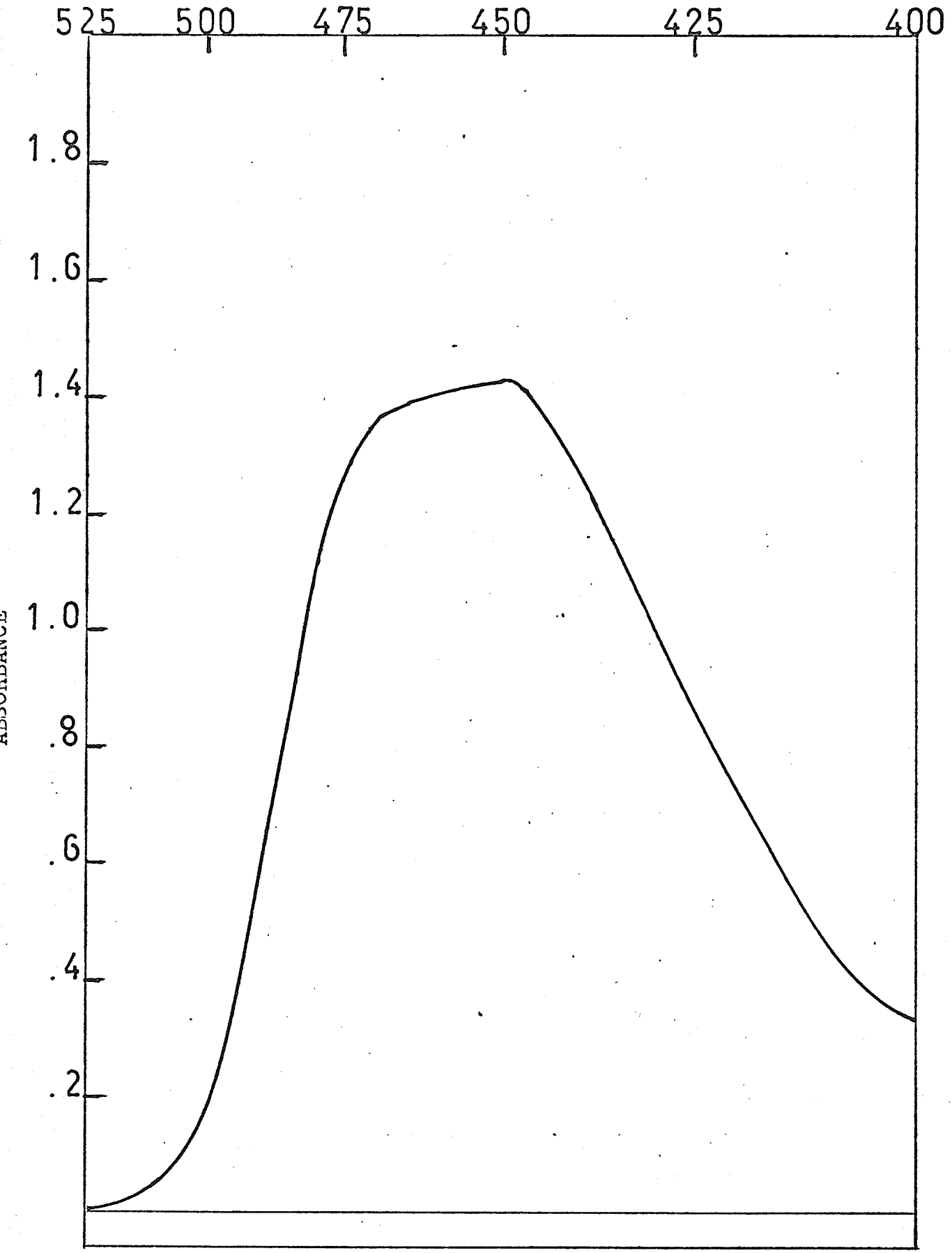

525
500
475
450
425
400
1.8
1.6
1.4
1.2
1.0
.8
.6
.4
.2
ABSORBANCE
WAVELENGTH IN nm.

FIGURE 9

in the yield of salicylic acid and a decrease in overall mass balance based on the aromatic moiety of E. It appears then, that under the conditions where anthranilic acid is formed, some other product besides salicylic acid is being formed.

Since not all of the products could be accounted for in the analysis, we decided to postpone kinetic studies and to look for reaction conditions which might optimize the yield of anthranilic acid. To do this, we increased the pH of the decomposition medium and increased the temperature to 100°C so that decomposition could go to completion in a convenient time period.

Table 2 gives a summary of the product yields at 100°C from pH

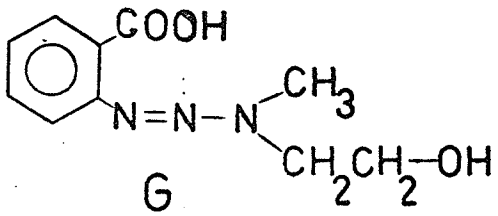
Table 2

pH	7.96	8.53	9.20
% yield anthranilic acid	5.7	19.0	22.5
% yield salicylic acid	78.0	50.0	35.0
Total mass balance	83.7	69.0	57.5

7.96 to 9.2. As before, the product distribution follows the same trend as a function of pH. But, if one compares the data of pH 7.96 at 50°C (Table 1) and 100°C (Table 2), one observes that the overall yield of anthranilic acid has decreased at 100°C and the overall yield of salicylic acid has increased at 100°C. It would appear from these product distribution studies that the reaction conditions most favorable for anthranilic acid formation are the lower temperature and slightly more alkaline reaction conditions.

In order to verify whether or not anthranilic acid could be formed from 2-carboxybenzediazonium ion F, a 5×10^{-2} M solution of F was decomposed at pH 8.5 and 100°C. Analysis of the decomposition mixture using the previously described method revealed the absence of anthranilic acid.

At this stage in the investigation, we could still not account for all the products of decomposition originating from the aromatic portion of E. From work done on another triazene (1-(2-nitrophenyl) -3,3-dihydroxyethyltriazene), we suspected that one of the products formed might be benzoic acid. However, its analysis by u.v. is subject to the same problems as those experienced for anthranilic acid and salicylic acid but no convenient colorimetric method could be found for benzoic acid analysis. Therefore, we selected a gas chromatographic procedure which has been reported by Manjarrez (22). From preliminary control experiments, we found that a 5% or less yield of benzoic acid could be detected if the initial concentration of E were of the order of 10^{-2} M. Compound E's limit of solubility in water is of the order of 2×10^{-3} M; therefore, another more soluble triazene had to be found for this experiment. The one selected was 1-(2-carboxyphenyl)-3-methyl-3 -hydroxyethyltriazene (hereafter to be called G).

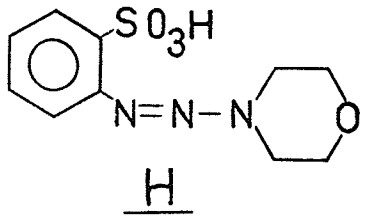


G

Two 50 ml samples of 10^{-2} M G were decomposed in sealed ampoules at 100°C to keep reaction times brief. One sample was buffered at pH 8.1 and the other at pH 8.95. After two days in the bath the ampoules were removed, extracted three times with ether and the ether extracts were concentrated down to 5 ml on a rotary evaporator. Samples from these extracts were injected in the gas chromatograph under conditions for which the retention time of benzoic acid was known. Using the most sensitive detection conditions on the instrument, no benzoic acid was found. Therefore, the aromatic moiety of the triazene is still not completely accounted for.

Because of this lack of mass balance we decided to extend the investigation to a substituent effect study. In other words, we wished to study if the nature of the substituent on the aromatic nucleous of diazoimino compounds affects the amount and types of products formed under different pH conditions.

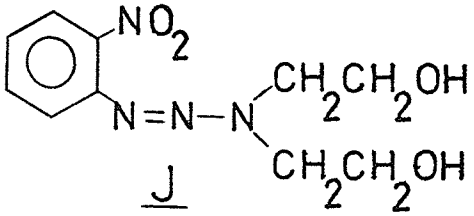
2. 1-(2-benzenesulphonic acid)-3-morpholinotriazene (H)



H

In view of the work reported by Petitcolas and Thirot (24) we thought it would be interesting to study the effect of a stronger acid substituent than the carboxyl group. Therefore H was synthesized and isolated as its sodium salt. However, the latter could not be purified and hence investigations based on it had to be abandoned.

3. 1-(2-nitrophenyl)-3,3-dihydroxyethyltriazene (J)



J

J was synthesized in the usual manner. Diethanolamine was used as the 2^{o} amine to insure 10^{-2} M solubility of J. Preliminary experiments showed that u.v. spectrophotometry could not be used as a tool for the product analysis of the decomposition of J since J absorbs at wavelengths where the expected products 2-nitrophenol and 2-nitroaniline absorb. These experiemnts also showed that the expected products do not form coloured species with ferric ion solution and PDAB solution respectively.

However, it was shown that the extent of reaction could be followed by measuring the absorbance of J at 270 nm.

As before, the decompositions of J were done in sealed ampoules at 100°C in an oil bath at various buffered pH's. After two days at 100°C the decomposition of J at pH 5 was only 75% complete and after six days at pH 6 the decomposition was only 61% complete.

From these observations, it is obvious that the effect of the electron-attracting nitro group is to slow down drastically the rate of decomposition of triazene by comparison with the ortho carboxyl group in E, since at these pH's the decomposition of E was usually complete after a few hours at 50°C. Also, one observes that the effect of pH on the decomposition of J is similar to that experienced in the decomposition of the 2-carboxyphenyltriazene E. That is to say, increasing the pH decreases the rate of decomposition.

The analytical method eventually selected for the product analysis of J was gas chromatography. Under the proper column conditions both of the expected products 2-nitroaniline and 2-nitrophenol gave suitable peak shapes and retention times. A trial decomposition of J at pH 5 showed the presence of 2-nitroaniline, nitrobenzene and traces of 2-nitrophenol. Evidence for these was established by comparison of their retention times with the retention characteristics of reference samples. Additional evidence was also acquired from analysis of the mass spectra produced by the various peaks in the chromatogram of the products.

Prior to investigating the quantitative distribution of the observed products, several control experiments were conducted to check out the analytical method to be used. Because these control experiments showed that the analytical method had some limitations, a brief resume of the analytical method used should be given. After a 10^{-2} M solution of

J in a buffer has spent a given number of days in an oil bath at 100°C, it is made basic with KOH pellets and extracted three times with equal volumes of chloroform to remove nitrobenzene and 2-nitroaniline. The chloroform extracts are concentrated down on a rotary evaporator to a final volume of approximately 5 ml and dried over $MgSO_4$. After filtering off the drying agent, a known amount of internal standard is then added to the chloroform extract, and the resulting mixture chromatographed. The basic aqueous extract is then made acidic and the same procedure repeated to remove the 2-nitrophenol.

In order to check the extractability of the expected products from water, u.v. concentrations (approximately 5×10^{-4} M) of 2-nitroaniline, 2-nitrophenol and nitrobenzene were made up in pH 6 buffer and the respective u.v. spectra recorded. Each solution was extracted three times with chloroform, and u.v. spectra of the aqueous phases were recorded again to see how much of the solutes were remaining in solution. For all three solutions the absorbance ot the respective peak maxima goes to zero after extraction. In other words, no solute remains in the aqueous phase.

So that the entire analytical method could be checked from start to finish, a reference mixture comprising the three expected products was made up in pH 6 buffer solution and 50 ml aliquots of it were subjected to the same procedure as a typical decomposition mixture would be subjected to. The concentration of the solutes in the reference mixture was 10^{-3} M with respect to each of the three solutes. This corresponds to a 10% yield of each solute in a decomposition mixture if the initial concentration of J were 10^{-2} M. Two ampoules labelled (a) and (b) respectively were filled with 50 ml aliquots of the reference mixture. These solutions were degassed by bubbling nitrogen through

them for twenty minutes and the ampoules were sealed under nitrogen. After six days in a 100°C both these solutions were analysed for the three solutes by the gas chromatographic method described above. Two more 50 ml aliquots labelled (c) and (d) respectively which were at room temperature for six days and exposed to the air were analysed in the same way. One more 50 ml aliquot, (e), identical to (c) and (d) was analysed in the same fashion except that the concentrating of the chloroform layers was done by flash distillation. Table 3 gives a

Table 3

Trial	a	b	c	d	e	average
% recovery o-nitrophenol		61.6	57.0		68.9	62.5
% recovery o-nitroaniline	83.0	84.6	88	78.5	84.0	83.6
% recovery nitrobenzene	52.2	55.8	72.1*	51.0	52.5	52.9

* c not included in average

summary of the percent recovery of each solute per trial analysis done.

From this Table several observations can be made. The first one is that the recovery of these components is far from quantitative. This is very surprising, since our previous extraction experiments followed by u.v. showed that none of the solutes remained in the aqueous layer after extraction. Thus far, no satisfactory explanations have been found to account for this discrepancy. Secondly, these results show that this discrepancy is not caused by the high temperature conditions, the presence of air or the method of concentrating the extracts. A third observation that can be made is that the percent

recoveries are fairly consistent, at least for 2-nitroaniline and nitrobenzene.

Fifty millilitre aliquots of 10^{-2} M J in buffered solutions were decomposed under nitrogen atmosphere at 100°C for seven days. Duplicate samples were decomposed at pH 5 and 6. The analysis was conducted as described above and the results are given in Table 4.

Table 4

pH	5	5	6	6
% decomposition	100	100	61	61
% yield o-nitrophenol	.5-1	.5-1	.5-1	.5-1
% yield o-nitroaniline	4.6	4.6	3.7	3.7
% yield nitrobenzene	41.7	42.0	29.5	29.5

The extent of reaction can be deduced from the u.v. absorbance of J at 270 nm before and after the six days in the oil bath. By applying the percentage recoveries obtained from the reference mixture study, one can approximate the actual yield of the products in the decomposition of J. In other words, if recovery were quantitative, the product distribution in the decomposition of J should be greater than those reported in Table 4. Table 5 then, summarizes the estimated yield for each of the products.

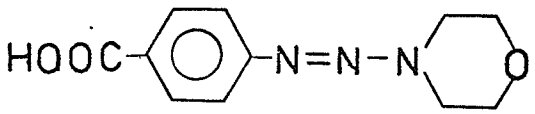
Table 5

pH	5	5	6	6
% yield o-nitrophenol	1.0	1.0	1.0	1.0
% yield n-nitroaniline	5.5	5.5	4.4	4.4
% yield nitrobenzene	79.4	79.4	55.7	55.7
Total % yield	84.9	84.9	60.1	60.1

One observes in Table 5 that if the decomposition at pH 6 were allowed to proceed to 100% reaction, the amount of 2-nitroaniline and nitrobenzene would exceed those amounts produced at pH 5. Table 5 also shows that as the pH of the medium is increased, the yield of 2-nitroaniline and nitrobenzene also increases.

Three other triazenes were also synthesized to study the effect of the aromatic substituent on the decomposition of diazoimino compounds. These are 1-(4-carboxyphenyl)-3-morpholinotriazene (K), 1-phenyl-3-morpholinotriazene (L), and 1-(2-methoxyphenyl)-3,3-dihydroxyethyltriazene (M). Unfortunately only qualitative information is available for K and L, and none is available for M.

4. 1-(4-carboxyphenyl)-3-morpholinotriazene (K)



K

Compound K was synthesized by the usual method using morpholine as the secondary amine of choice to insure sufficient solubility of K in water. Preliminary experiments showed that the colorimetric test described for anthranilic acid works also for p-aminobenzoic acid. The resulting spectrum of the coloured complex appears in Fig. 10. Solutions of K (10^{-2} M) were decomposed at 100°C in an oil bath, in buffered solutions of pH 7.23 for one day and pH 9.85 for 12 days. Upon removing the decomposition mixture from the bath we observed that the solution had a yellow colour and therefore, a special precaution was taken in preparing the solutions for the u.v. reference and sample cells. The sample solution was made up with 5 ml of decomposition

FIGURE 10

Spectrum of p-aminobenzoic Acid plus PDAB

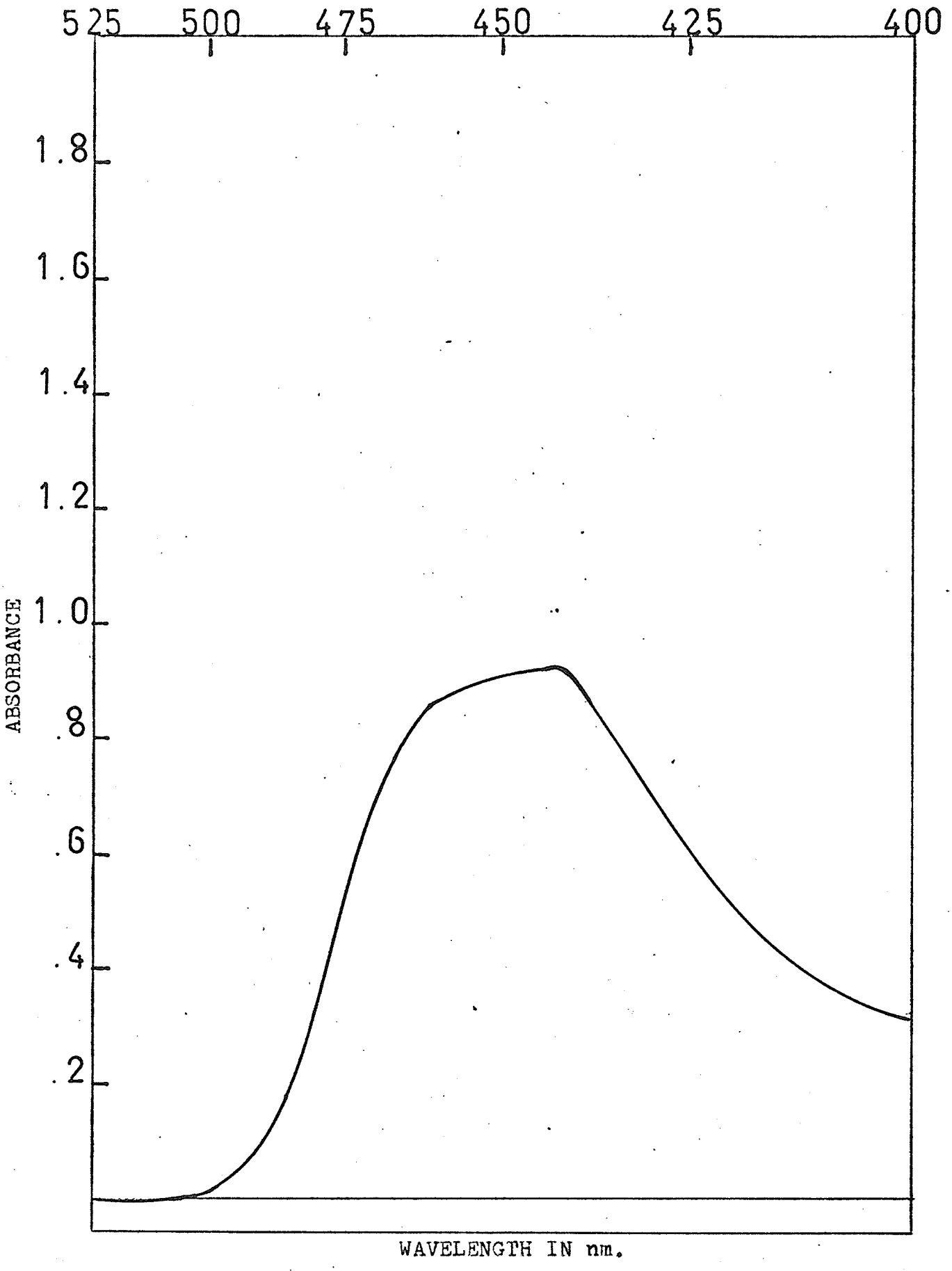
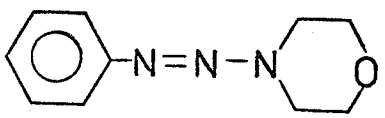

525
500
475
450
425
400
1.8
1.6
1.4
1.2
1.0
.8
.6
.4
.2
ABSORBANCE
WAVELENGTH IN nm.

FIGURE 10

mixture plus 1 ml of PDAB and the reference solution contained 5 ml of decomposition mixture plus 1 ml of water. Fig. 11 shows the sprectrum of the coloured complex obtained from a pH 7.23 decomposition. An identical spectrum was observed for a pH 9.85 decomposition. Fig. 12 shows a spectrum of PDAB in the wavelength region of interest. From it one can estimate the PDAB contribution to the absorbance at 445 nm in the spectrum of Fig. 11. From Fig.'s 10 to 12 one can conclude that the decomposition of K leads to the formation of primary amine under the reaction conditions described avove. Since the extent of reaction for this decomposition is unknown, this represents a minimum yield of approximately 10%.

In view of the fact that the sum of the product yields from a similar triazene E never approached 100%, it was not considered profitable to do a more quantitative study of K.

5. 1-phenyl-3-morpholinotriazene (L)



L

Compound L was synthesized in the usual manner using morpholine as the secondary amine of choise to insure sufficient solubility of L. Solutions of L (10^{-3} M) in buffers of pH 3.85, 7.23 and 9.85 were decomposed in a 100°C oil bath for twenty-four hours. At pH 3.85 and 7.23 the reaction was complete since the absorbance for L at 310 nm had gone to zero. For pH 9.85 however, the extent of reaction was only about 50% complete after one day in a hundred degree bath. At the lowest pH studied, the only product of decomposition present was phenol

FIGURE 11

Spectrum of Decomposition Product of K plus PDAB

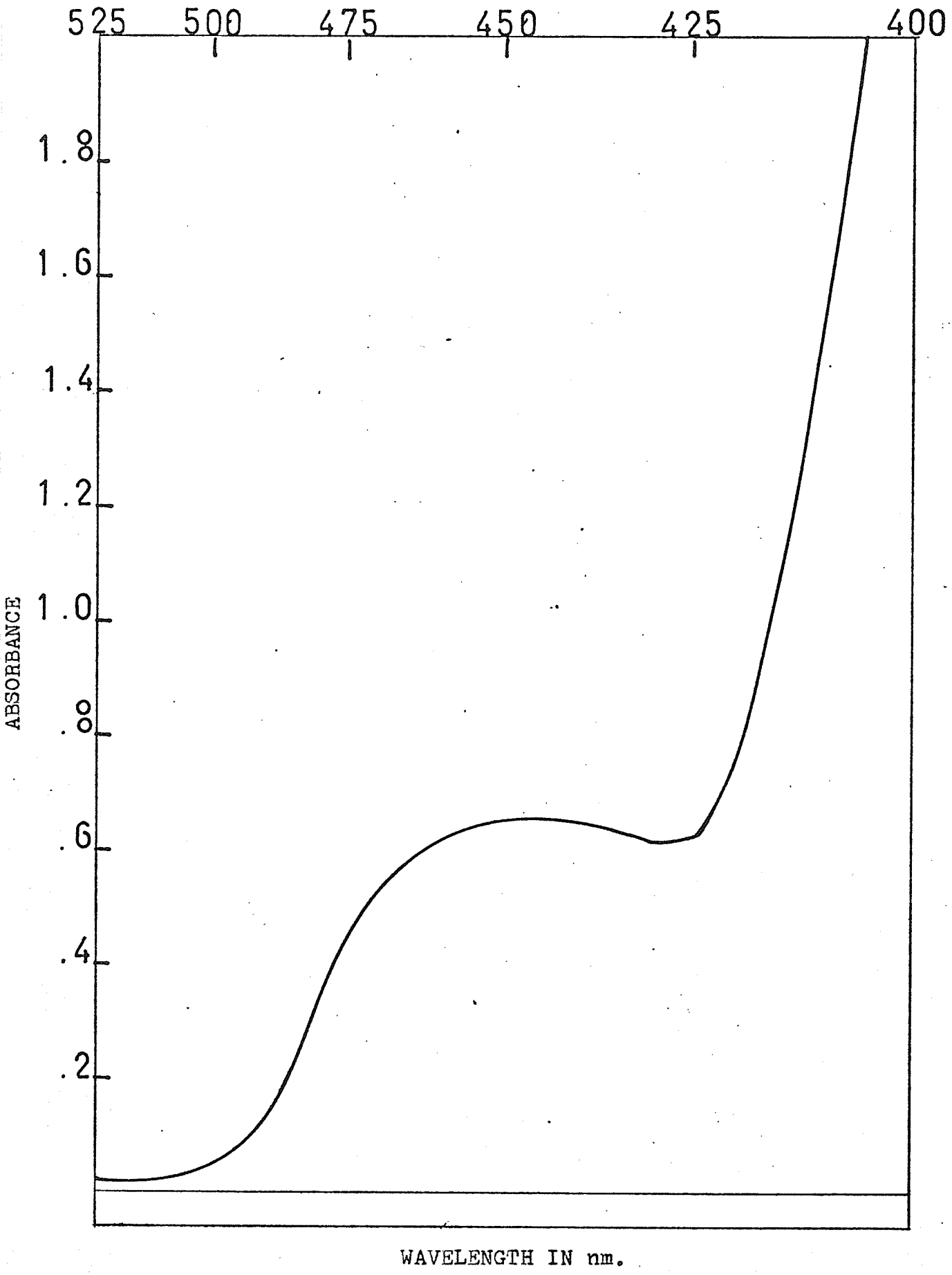

525
500
475
450
425
400
1.8
1.6
1.4
1.2
1.0
.8
.6
.4
.2
ABSORBANCE
WAVELENGTH IN nm.

FIGURE 11

FIGURE 12

Spectrum of PDAB

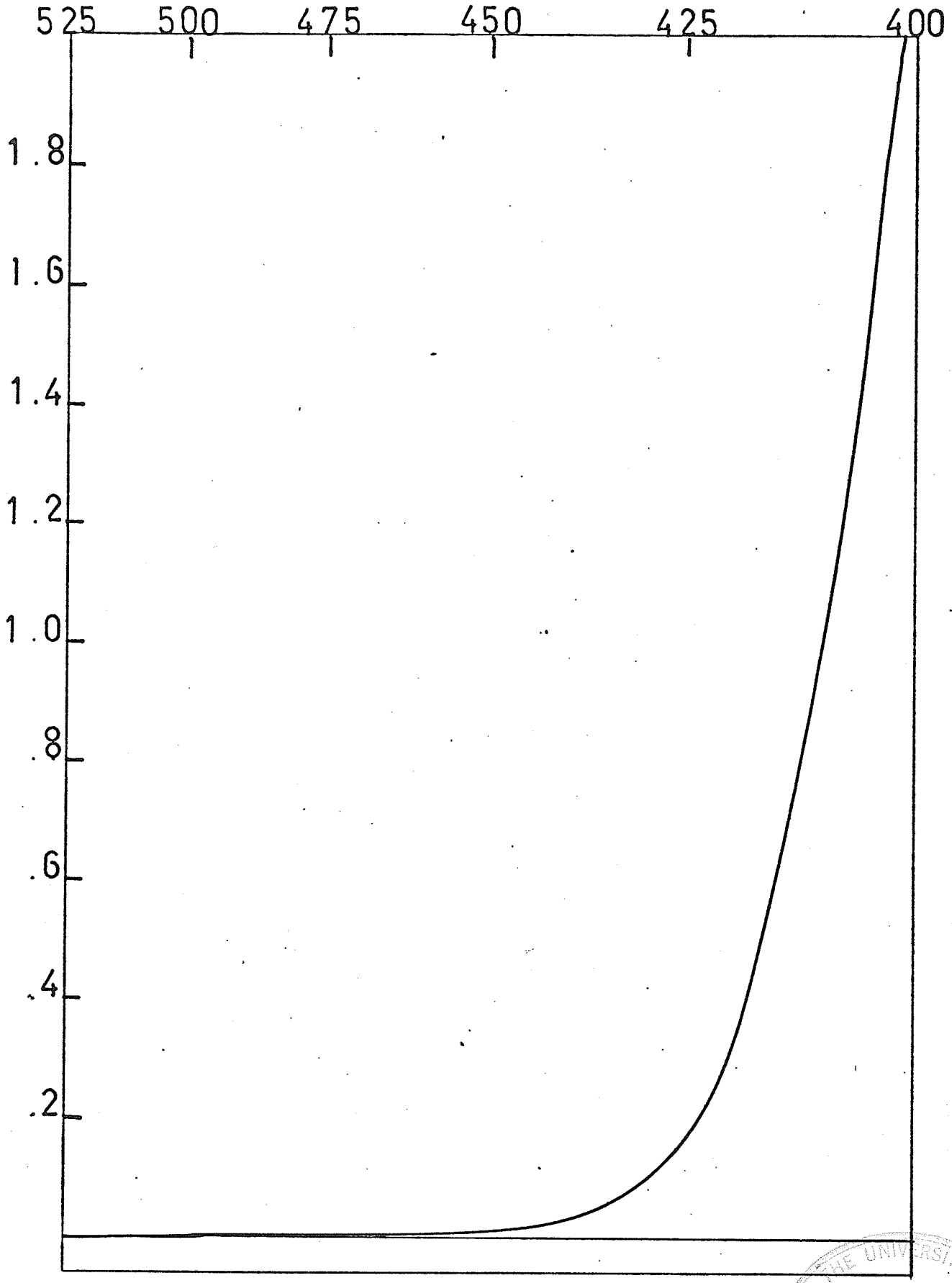


FIGURE 12

as identified by its u.v. spectrum and by the colorimetric method described for anthranilic acid. A test of the decomposition mixture for aniline with PDAB gave negative results. At pH 7.23 the product of decomposition was not readily identifiable from the u.v. spectrum, but a test with PDAB also gave negative results. A similar result was observed at pH 9.85.

To insure that the PDAB test was sensitive enough to detect appreciable percentages of aniline if it were formed, an aqueous aniline solution (5×10^{-5} M) was mixed in the usual manner with PDAB solution to give an absorbance reading of .2 at 425 nm. Since the initial concentration of L was 10^{-3} M, this corresponds to a 5% or less reaction which could have been detected.

V. CONCLUSIONS

The conclusions which can be drawn from the above results section may be summarized as follows:

1. 1-(2-carboxyphenyl)-3-piperidinotriazene (E)

a) From the spectral studies of E decomposing as a function of time one observes in a qualitative fashion that the pH rate profile follows that reported by Dayal (10) Fig. 1. However, the rate begins to fall off rapidly above pH 6.

b) In the pH region where the rate of decomposition is decreasing (at pH 6), an increase in pH increases the yield of anthranilc acid, decreases the yield of salicylic acid and decreases the overall yield of products.

c) For a given pH, increasing the decomposition temperature decreases the yield of anthranilic acid and increases the yield of salicylic acid.

d) Although the experiment could not be done using compound E, results obtained with G shows that no benzoic acid is formed. If we can assume that the nature of the secondary amine comprising the imino portion of diazoimino compounds does not affect the product distribution for the aromatic moiety, we can say that no benzoic acid is formed from the decomposition of 2-carboxyphenyltriazenes.

2. 1-(2-nitrophenyl)-3,3-dihydroxyethyltriazene (J)

a) The ortho nitro group appears to slow down drastically the decomposition of triazene by comparison with the ortho carboxyl group.

b) In the pH region studied, the rate of decomposition of J decreases with increasing pH.

c) Increasing the pH increases the yield of both 2-nitroaniline and nitrobenzene.

3. 1-(4-carboxyphenyl)-3-morpholinotriazene (K)

At pH's greater than 7, p-aminobenzoic acid is formed from K.

4. 1-phenyl-3-morpholinotriazene (L)

No aromatic amine was observed in the pH region 7 to 10.

In addition to the above conclusions, it can be shown in a qualitative fashion from the observed reaction times that the various substituents on the aromatic portion of diazoimino compounds increase the rate of decomposition in the following order of substituents: 2-COOH > 4-COOH > H > 2-nitro. Also, for those triazenes where primary amine was formed, the yields of primary amine increase in the following fashion: 2-COOH > 4-COOH > 2-nitro.

At first sight, it would appear that the absolute yields of aromatic amine can be correlated with the rates of decomposition, since the yields of aromatic amine and the rates of decomposition increase in the same order of substituents. However, in the case (E) where the rate of decomposition was increased by increasing the temperature of the reaction, it was observed that the yield of aromatic amine decreased. Therefore, there appears to be no simple correlation between rate and yield.

One also observes that in the pH regions where aromatic amine is formed, the rate of decomposition is decreasing as a function of increasing pH. Further more, an increase in pH increases the amount of aromatic amine formed.

For all the triazenes studied, except the 2-nitrophenyltriazene, the formation of the corresponding phenol from the aromatic portion of the triazene appears to be an important reaction pathway. Its formation can be rationalized following Petitcolas and Thirot (24): first, protonation at N_3 to give a protonated species; secondly, the dissociation

of the protonated species into diazonium ion and secondary amine; finally, the reaction of the diazonium ion with water to give phenol and nitrogen.

On the other hand, the formation of deamination product appears to be the favoured reaction pathway for the decomposition of the 2-nitrophenyltriazene, since high yields of nitrobenzene were observed. This fact can best be rationalized if one recalls the work of Andakushkin (2) (Page 9 this thesis), who found that the diazohydroxide formed from the decomposition of triazenes can dissociate into organic radical and OH radical plus nitrogen. Other reports (4,7,29) exist in the literature stating that benzenediazonium ions decompose in alkaline media via a free radical mechanism to give aryl radical. It has also been reported (4) that in the presence of "alphatic hydrogen-containing compounds", these aryl radicals may abstract hydrogen atoms to give the appropriately substituted benzenes according to:

$$Ar\cdot + R\text{-}H \longrightarrow Ar\text{-}H + R\cdot$$

The only such source of aliphatic hydrogen available in our systems are the secondary amines which are formed in the decomposition of triazenes.

From the previously stated conclusions and observed product distributions, it is obvious that the decomposition of diazoimino compounds in the weakly acidic to weakly basic pH region is very complicated. In some cases, primary aromatic amine and phenol are major products, and in other instances, primary aromatic amine and deamination product are predominant. In addition, the gathering of information for these systems is further complicated by the fact that

the analytical methods required are varied, long and tedious.

It is probable that the observed product distributions result from a set of parallel competing reactions, each of which can be influenced in different ways depending on the reaction conditions used and the type of substituent on the aromatic portion of the triazenes studied. However, no direct evidence exists for these competing pathways from this study. The ultimate sorting out of these pathways would no doubt be a lengthy and difficult project.

With regard to Dayal's mechanism for the decomposition of triazenes, the present work does not shed much more light on the mechanism of formation of primary aromatic amine. However, it has become obvious that the pathway leading to phenol formation must be included for those triazenes studied which gave the appropriate substituted phenol. The work of Taylor (30) also casts some doubt on the formation of N-nitroso compound as a final product in the decomposition of triazenes. In view of the complexities we have encountered in the decomposition of triazenes it appears that the elucidation of Dayal's mechanism will be laborious and difficult.

VI. EXPERIMENTAL

A. Synthesis of Diazoimino Compounds

1. General method and materials

The diazoimino compounds used were synthesized by the general method of Rondestvedt and Davis (25) which involves the nitrogen coupling of the diazotized aromatic amine to the secondary amine in a basic sodium carbonate solution. All the aromatic and secondary amines were commercially available samples and all were used without further purification.

The purity of all the reference compounds used for u.v. calibration graphs was checked by determination of their respective melting points. Those compounds whose purity was questionable were purified by some suitable method described in the appropriate section below.

The purity of the internal standards and the reference compounds used in the chromatographic analysis was checked by determination of their respective melting points and the lack of extraneous peaks on their respective chromatographic traces. Where applicable, the particular impure compound was purified by a suitable method to be described in the appropriate section.

NOTE - All melting points were taken on a calibrated Fisher Johns apparatus.

2. 1-(2-carboxyphenyl)-3-piperidinotriazene (E)

Anthranilic acid (12 g) was dissolved in a mixture of concentrated HCl (10 ml) and water (30 ml). After adding ice (25 g) and more HCl (7.5 ml) to the above solution, it was cooled to 0-5°C using an ice bath. To this solution was added slowly dropwise a cold solution of sodium nitrite (7.2 g) in water (14 ml) till an excess of nitrous acid was present. The presence of nitrous acid was detected using potassium iodide-starch paper which turned dark blue immediately on contact with

the solution containing unreacted nitrous acid. The excess nitrous acid was decomposed by adding a few crystals of sulphamic acid to the reaction mixture and the solution was checked again with potassium iodide-starch paper till no colour change was observed.

A solution of piperidine (8.5 g, 0.1 mole) in water (100 ml) containing an equimolar amount of sodium carbonate (28.6 g) was cooled to 5-10°C using an ice bath. The diazonium solution prepared above was added rapidly dropwise during about 10-20 minutes to this alkaline solution of piperidine. After stirring this reaction mixture for .5 hours at 5-10°C, it was acidified carefully with 6 M HCl till E precipitated from solution. The crude product was filtered on a Büchner funnel, washed several times with cold water and dried. The crude triazene was recrystallized twice from methanol giving 7.5 g of pale yellow needles m.p. 86-87°C. The structure E was established by elemental analysis (see Table 6) and mass spectrometry (m.s.). The predominant m/e values are: 233, 149, 121, 85, 84.

3. 1-(2-nitrophenyl)-3,3-dihydroxyethyltriazene (J)

Compound J was synthesized in the same fashion as E except that crude J precipitates from solution at the coupling stage. The crude product was filtered, washed several times with water and dried. After treatment of a benzene solution with charcoal, the crude product was recrystallized twice from benzene giving bright yellow needles m.p. 64-65°C (see Table 6). The predominant m/e values are: 254, 237, 181, 150, 138.

4. 1-(4-carboxyphenyl)-3-morpholinotriazene (K)

Compound K was synthesized in the usual manner except the sodium salt of K precipitates out of solution at the coupling stage. The solution was filtered on a Büchner funnel and the salt was redissolved

in a minimum amount of distilled water and acidified carefully with 6 M HCl. Crude K precipitated from solution, was filtered on a Büchner funnel and washed several times with cold water. The crude product was recrystallized several times from 95% ethanol giving 12 g of fine white crystals, m.p. 205-206°C (see Table 6). The predominant m/e values are: 149, 121, 103, 93, 76.

5. 1-phenyl-3-morpholinotriazene (L)

Compound L was prepared in the usual manner and it precipitated from solution at the coupling stage. The crude product was filtered and washed several times with cold water. Compound L was observed to be a low melting material and all attempts to recrystallize it resulted in the separation of an oil. Attempts to purify L by vacuum distillation failed since the heat required caused rapid decomposition of the compound. Finally, L was placed in a sublimation apparatus and the latter was evacuated to a pressure of 15 mm Hg pressure using a water aspirator. The bottom of the sublimation apparatus was heated gently using a heating mantle until the vapours of L began to condense on the cold finger. The yield of crude product was almost quantitative but only a sufficient amount of L was purified for the decomposition trials and the structure determination. The pure product crystals are pale yellow needles m.p. 25.6-26.6° (see Table 6). The predominant m/e values are: 191, 105, 77, 51, 28.

6. 1-(2-benzenesulphonic acid)-3-morpholinotriazene (H)

Compound H was synthesized in the usual manner. Attempts to induce precipitation of the free acid by acidifing an aliquot of the reaction mixture with 6 M HCl failed. This acidified aliquot was also extracted several times with various organic solvents but subsequent

evaporation of the extracts yielded no organic material. Finally, the aqueous reaction mixture was evaporated on a rotary evaporator at a pressure of 0.1 mm Hg. The inorganic salts which remained behind were washed several times with absolute methanol on a Büchner funnel. Evaporation of the washings on a rotary evaporator yielded 10 g of solid organic material. Its u.v. spectrum showed similar absorption characteristics to those obtained from previously studied triazenes. Comparison of the u.v. spectrum of starting material showed that the organic material recovered was not starting material. Therefore, we concluded that the organic material recovered was the sodium salt of H since the m.p. of this organic material is greater than 300°C. However, all attempts to purify this salt by sublimation or recrystallization failed.

7. 1-(2-methoxyphenyl)-3,3-dihydroxyethyltriazene (M)

Compound M was synthesized in the usual manner and crude M precipitates from solution at the coupling stage. Crude M was recrystallized four times from a benzene-petroleum ether solution giving 12 g of fine white crystals, m.p. 69-70.5° (see Table 6). The predominant m/e values are: 239, 166, 137, 123, 77.

TABLE 6 DIAZOIMINO COMPOUNDS USED

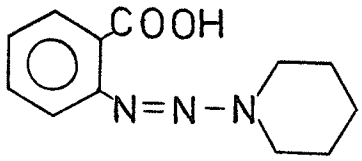
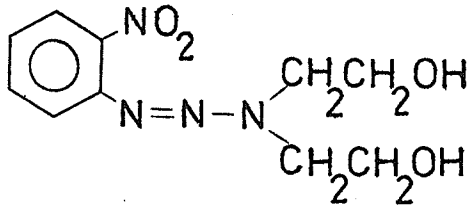
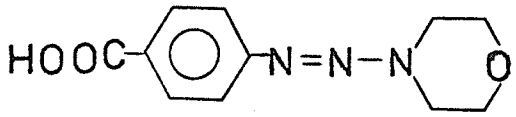
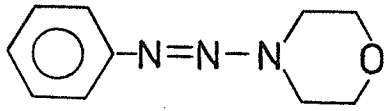
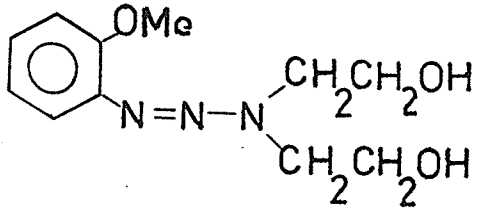
Name	Formula	Mole wt.	m.p.	Calc. found	Analysis C %	H %	N %
1-(2-carboxyphenyl)-3-piperidinotriazene		233.14	87°	Calc. found	61.76 61.85	6.48 6.53	18.02 18.12
1-(2-nitrophenyl)-3,3-dihydroxyethyltriazene		254.14	65°		47.22 47.10	5.55 5.63	22.05 22.16
1-(4-carboxyphenyl)-3-morpholinotriazene		235.13	206°		56.14 56.30	5.57 5.70	17.87 18.03

TABLE 6 cont'd

Name	Formula	Mole wt.	m.p.	Calc. found	C %	H %	N %
1-phenyl-3-morpholinotriazene		191.13	26.6°	Calc.	62.78	6.86	21.99
				found	62.72	6.90	22.08
1-(2-methoxyphenyl)-3,3-dihydroxyethyltriazene		239.19	70.5°		55.19	7.16	17.57
					55.32	7.31	17.78

B. Buffer Solutions

Buffer solutions were prepared as suggested by Bates (5) and/or Britton (6) using HCl and sodium acetate to buffer the pH region 1-5, sodium hydrogen succinate plus sodium succinate in the pH region 5-6, and boric acid plus borax in the pH region 7-9. The ionic strength of the medium was adjusted to 0.2 with KCl. All pH measurements were made with a Radiometer Model 4C pH meter using shielded glass (G 202 B) and calomel (K 100) electrodes at room temperature. The meter was calibrated at 25°C with either .05 M tetroxalate, .05 M potassium hydrogen phthalate or .01 M borax depending on the pH region of interest.

C. Product Analysis

1. 1-(2-carboxyphenyl)-3-morpholinotriazene (E)

Compound E was allowed to decompose at room temperature, in a spectrophotometer call and the spectrum of the reaction mixture was scanned at various intervals of time. Compound E (0.145 g) was dissolved in 250 ml of 0.1 N NaOH to give a final concentration of 2.5×10^{-3} M in E. The spectra in Fig.'s 2-3 were produced by scanning, immediately after mixing, a solution of E (0.1 ml delivered with a 100 ul syringe) with 2.5 ml of appropriate buffer already contained in a 1 cm quartz u.v. cell. The reference cell also contained the same buffer as in the sample cell. All u.v. spectra were scanned on a Perkin Elmer Model 450 spectrophotometer, and all absorbance measurements at fixed wavelength were done on a Beckman D.U. spectrophotometer.

The spectrum of 2-carboxybenzenediazonium salt (F) in Fig. 7 was recorded after diluting an aliquot of cold 5×10^{-2} M F with 3 M HCl until its absorbance became measurable in the u.v. region.

Another aliquot (4 ml) of the same solution (5×10^{-2} M F) was added to 96 ml of pH 8.5 buffer which had previously equilibrated in a 100°C oil bath for one half hour. After six hours in the bath, the decomposition mixture was analysed for anthranilic and salicylic acid using the usual methods but only the test for salicylic acid was positive (80% yield).

Prior to doing product analyses on the decomposition mixture of E, calibration graphs of the expected products were constructed. The anthranilic and salicylic acids used for calibrating purposes were used as received since both had narrow melting point ranges. The p-dimethylaminobenzaldehyde (PDAB) was purified by eluting a benzene solution of it through a column of activated alumina. The solvent

was collected and concentrated on a rotary evaporator. Crystallization was induced by adding petroleum ether (b.p. 40-60°C) to the benzene solution of PDAB. The resulting crystals were filtered on a Büchner funnel, dried and gave a melting point of 74-75°C. The reagent PDAB solution was prepared by dissolving 60 mg of PDAB per millilitre of 3N H_2SO_4. the reagent solution for the salicylic acid analysis was prepared by dissolving $FeCl_3$ (10 g) in 1 l. of 0.1 M HCl.

For the calibration graph of anthranilic acid, solutions containing known concentrations of the acid were made up. Five ml of a given concentration were mixed with 1 ml of the PDAB reagent and the resulting absorbance read at 450 nm. Fig. 13 shows a typical calibration for anthranilic acid.

For the calibration graph of salicylic acid, a slightly different approach had to be taken due to the pH sensitivity of the method. This time, the solutions containing known concentrations of salicylic acid were made up in the same buffer to be used for the decomposition of E. The reason for this was that 2 ml of calibrating solution plus 5 ml of $FeCl_3$ solution would have the same resulting pH as 2 ml of decomposition mixture plus 5 ml of $FeCl_3$ solution. Hence, prior to each decomposition of E at a new pH, a new calibration graph of salicylic acid had to be constructed. A typical calibration graph for salicylic acid is shown in Fig. 14.

Compound E was decomposed at several pH's at 50°C and at 100°C in reaction vessels equipped with reflux condensers. Four ml of a 5×10^{-2} M stock solution of E (in 0.1N NaOH) were added to 96 ml of buffer which had previously equilibrated in the temperature bath for one half hour. After the reaction was complete, two aliquots of reaction mixture were mixed with the respective colorimetric reagents

FIGURE 13

Calibration Graph for Anthranilic Acid

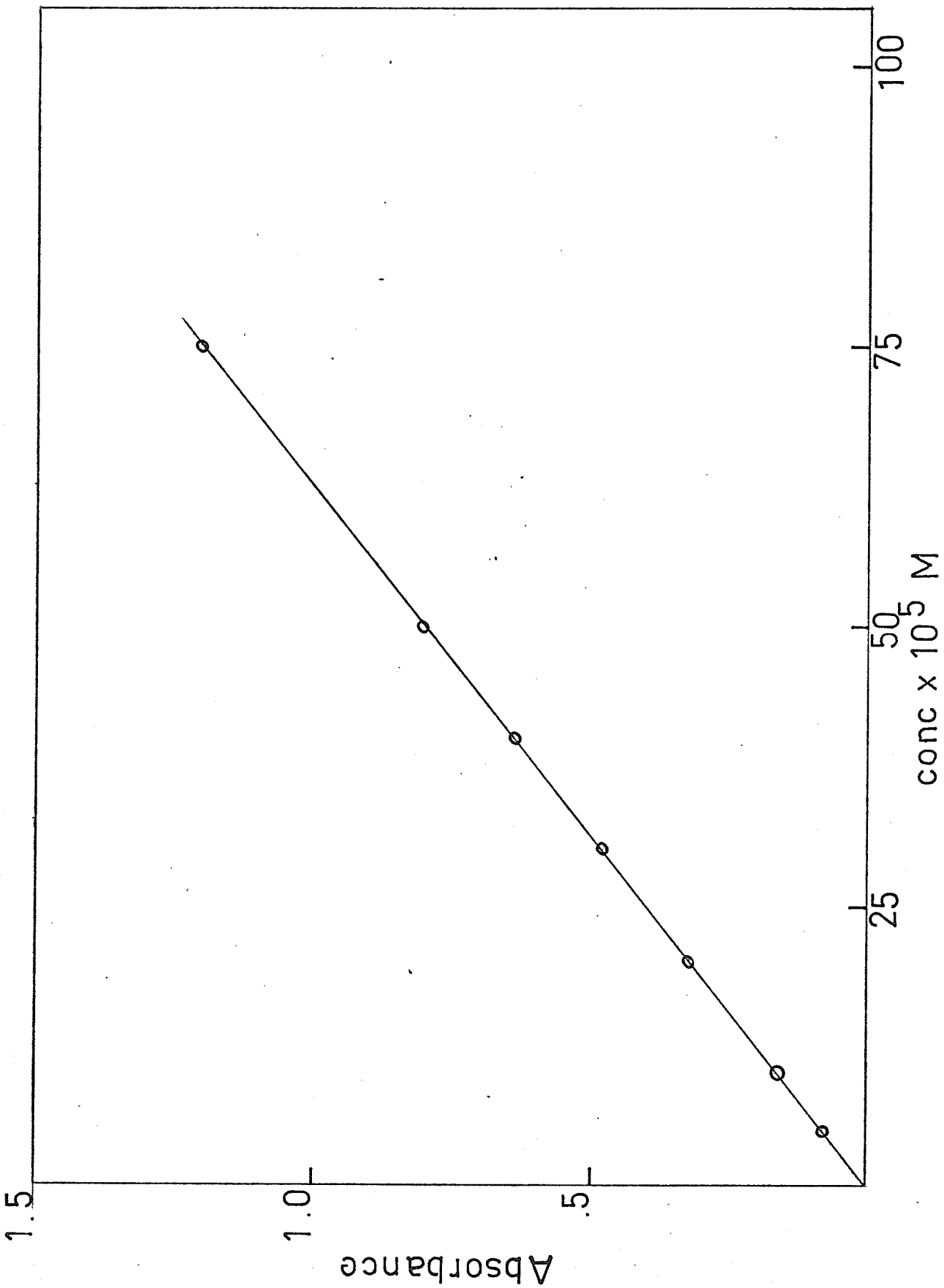


FIGURE 13

FIGURE 14

Calibration Graph for Salicylic Acid

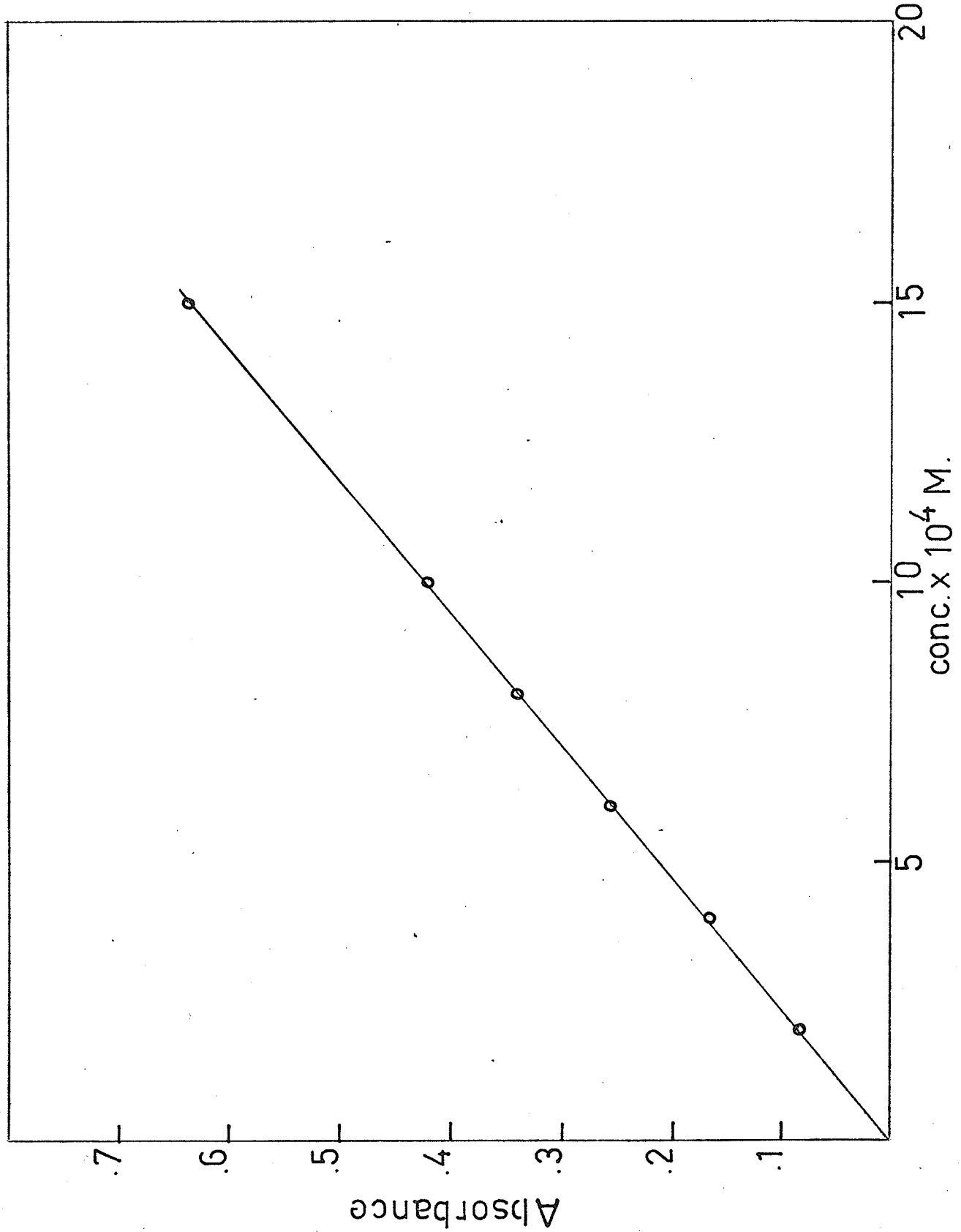


FIGURE 14

and the absorbance read immediately at 450 nm for anthranilic acid and 525 nm for salicylic acid. The absorbance of the respective products was used in conjunction with the calibration graphs to determine the concentrations of these products. This procedure was repeated at various time intervals near the end of the reaction till the absorbance of both products remained constant. That is to say, the reaction was complete.

2. 1-(2-nitrophenyl)-3-dihydroxyethyltriazene (J)

The analysis of the products in the decomposition of J was done on a Hewlett-Packard Model 700 gas chromatograph (g.c.) using dual flame ionization detectors.

The column used was a glass column having dimensions of 2m X 2mm It was filled with an inert support called Chromosorb W-AW 45/60 mesh size which had previously been coated with 10% by weight Carbowax 20M liquid phase. The column packing was prepared by dissolving the liquid phase (1g) in chloroform (50 ml). To this solution was added the inert support (9 g) and the solvent was removed slowly on a rotary evaporator in order to coat the inert support evenly with the liquid phase. A glass wool plug was inserted at one end of the column and a gentle vacuum applied to the same end while the coated support was introduced at the other end of the column by means of a small plastic funnel. After the column was filled, a glass wool plug was inserted into the inlet end of the column was then mounted into the g.c. oven. Prior to using the column on a routine basis, it was conditioned in the oven at 215°C overnight.

For all the analyses, the injector temperature was set at 110°C, the detector at 210°C and the inlet pressure regulated at 22 p.s.i. for the carrier gas. Since the instrument is not capable of linear temperature

programming, all these products had to be analysed at different oven temperatures. For nitrobenzene the oven temperature was set at 105°C, for o-nitrophenol at 115°C and for o-nitroaniline at 185°C.

The method which was used for the quantitative analysis of these products is called the internal standard method. Standard stock solutions of internal standard and a given component were prepared separately in absolute methanol. Solutions containing known weight ratio of the sample and the internal standard were prepared by delivering known volumes of each stock solution with an automatic burette. Each volume delivered was subsequently weighed on an analytical balance to insure the accuracy of the weight ratio. Each calibrant solution whose weight ratio of solutes was accurately known was chromatographed three times by injecting 1 ul samples on the column three times. Each injection yields two peaks, one for the sample and one for the internal standard. Each peak area was measured three times with a Hughes-Owens Zero Setting Compensating Planimeter and the average of the three readings was used in the area ratio determination. All three injections for a given calibration point on the calibration graph were measured in this way and the average of the three area ratios was used to fix this given calibration point on the graph. A typical calibration graph is given in Fig. 15 showing the area ratio of sample to standard on the ordinate axis versus the weight ratio of the sample to standard on the abssica.

The internal standards used for o-nitroaniline, nitrobenzene and o-nitrophenol were phenanthrene, p-nitrotoluene and ethyl benzoate respectively.

To check the overall analytical procedure including extraction, a synthetic mixture containing 10^{-3} M nitrobenzene, 10^{-3} M o-nitroaniline

FIGURE 15

Typical Calibration Graph for ONA demonstrating the Internal Standard Method

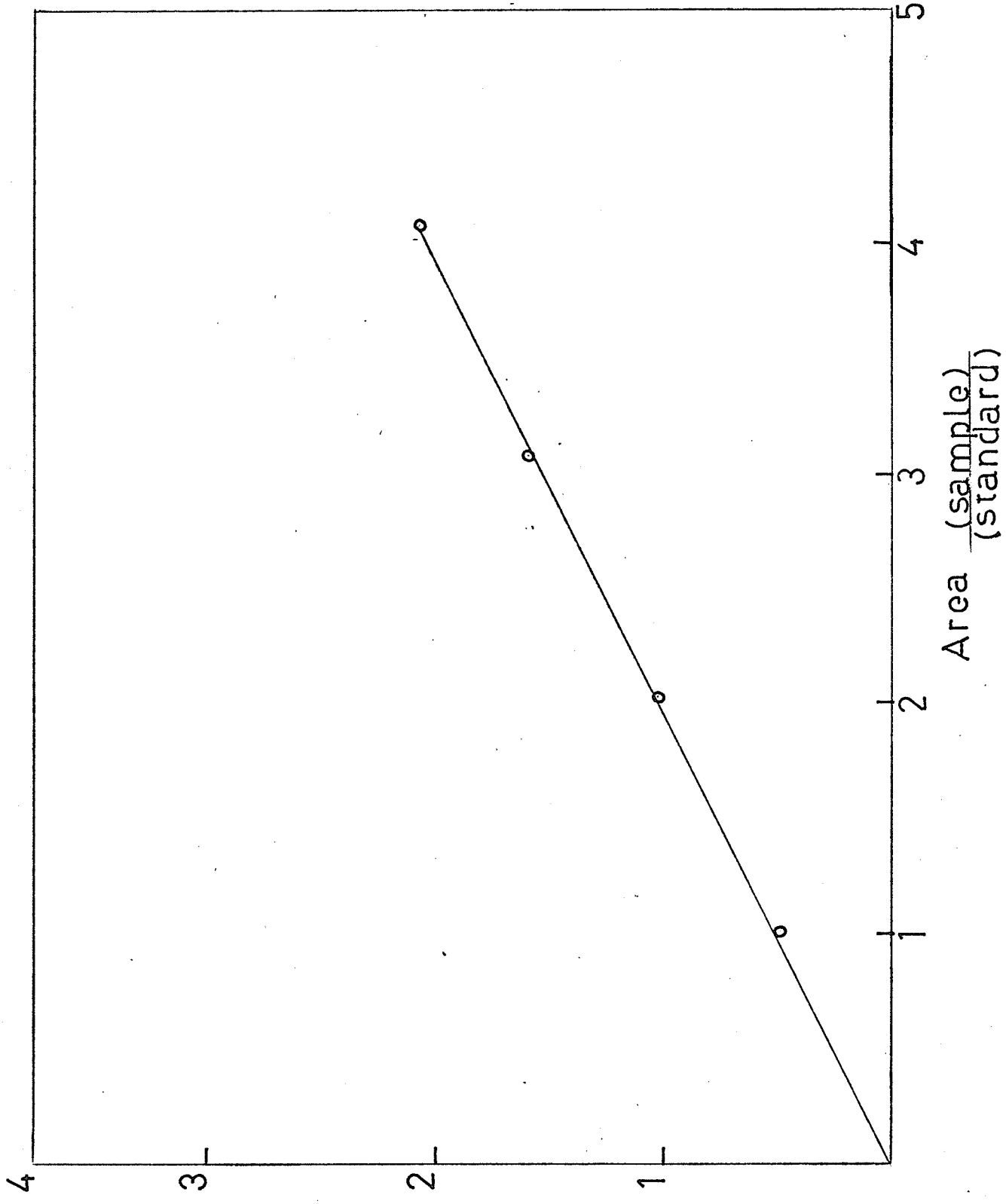


FIGURE 15

and 10^{-3} M o-nitrophenol in one litre of pH 6 buffer was prepared. Fifty ml aliquots were made basic with KoH pellets, extracted three times with equal volumes of chloroform and the chloroform extracts were concentrated on a rotary evaporator. A known amount of internal standard was added to this solution and the resulting mixture was chromatographed three times and the peaks were measured as in the calibration. Since the area ratio was measured and the amount of internal standard added was known, the calibration graph was used to find the amount of a given component actually in the sample. The aqueous layer from the above extraction was made acidic and the entire procedure repeated for it. From the basic extraction, o-nitroaniline and nitrobenzene were isolated and from the acidic extraction, o-nitrophenol was isolated.

For the decomposition of J, 50 ml aliquots of 10^{-2} M J were placed in ampoules and degassed for twenty minutes using dry oxygen-free nitrogen gas. The ampoules were sealed under nitrogen and placed in a 100°C oil bath for seven days. The product analysis for J was done in exactly the same manner described above for the synthetic mixture.

The three products were identified by comparing their g.c. retention times and mass spectra with the retention times and mass spectra of authentic samples.

3. 1-(4-carboxyphenyl)-3-morpholinotriazene (K)

Compound K (0.0237 g) in 100 ml aliquots of buffers pH 7.23 and pH 9.85 were decomposed for 12 days in a 100°C oil bath. The spectrum in Fig. 11 was prepared by putting a solution of 5 ml decomposition mixture of K plus 1 ml of PDAB reagent in the sample cell and 5 ml decomposition mixture plus 1 ml of water in the reference cell. The reason for putting decomposition mixture in both the sample

and reference compartments was to avoid interference of the yellow colour present in the decomposition mixture.

4. 1-phenyl-3-morpholinotriazene (L)

Compound L (0.0191 g) in 100 ml aliquots of buffers having pH 3.85, 7.23 and 9.85 respectively were decomposed in a 100°C oil bath for twenty-four hours. The colorimetric test for aniline using PDAB reagent was performed in the usual manner by mixing 5 ml of decomposition mixture plus 1 ml PDAB for the sample compartment of the spectrophotometer and placing a solution of 5 ml appropriate buffer plus 1 ml of water in the reference compartment and scanning the u.v. spectrum.

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