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SESSION D-IV-1

TITLE: Effect of Ionizing Radiation on Pyridine
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ABSTRACT: Pyridine, like benzene, has the resonating π -electron structure identified with aromatic compounds. Polar contributions due to the nitrogen atom in the pyridine ring are also present. Gamma irradiation (2.5×10^{22} electron volts/liter or 2.7×10^7 roentgens) of pure dried, oxygen-free, liquid pyridine resulted in negligible gas yields, but in measurable amounts of non-gaseous products. Analysis of these products by gas chromatography and ultraviolet absorption spectroscopy revealed the formation of 2,2'-bipyridine, 2,x'-bipyridine (either or both 2,3'- and 2,4'-bipyridine), and approximately an equal amount of an unidentified product. The total yield of a non-gaseous product from pyridine approximates that for benzene, demonstrating that pyridine behaves essentially as an aromatic when irradiated, and is relatively stable to radiation. The contribution of the presence of the N-atom is noted in the bipyridine isomers formed, and in the distribution of products. The bipyridine fraction of the total product is much greater than the biphenyl fraction from benzene.

As an aromatic compound, but one that is easily compatible with both organic and inorganic compounds, we anticipate that the pyridine molecule may be incorporated in systems where radiation protection or stability is desired. A mechanism based on the formation of free radicals is presented for the chemical effects of radiation on pyridine.

EFFECT OF IONIZING RADIATION ON PYRIDINE

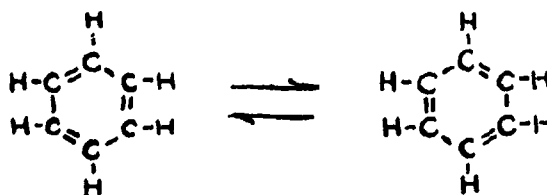
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INTRODUCTION

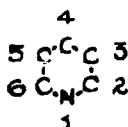
Protection against radiation damage is frequently observed in systems containing benzene or a benzene derivative. The cyclohexane-benzene system (1), where hydrogen and polymer formation from cyclohexane is reduced by the presence of benzene, is well known. Styrene and phenol polymers are relatively stable to radiation. Recently the use of benzene additives to stabilize plastics to radiation damage has been described (2). As a medium for the transfer of excitation energy due to irradiation of solutions, benzene and its derivatives are widely used in liquid scintillators. In fact, the scintillating compound itself may be a benzene derivative such as anthracene or terphenyl. Finally, these benzene compounds are characterized by a relatively low amount of change due to ionizing radiation, compared to other classes of chemical compounds.

Explanations of the resistance of benzene compounds to radiation-induced change, and of the radiation protection and energy transfer mechanisms involve their aromatic structure of six resonating π electrons, i.e.



In the structures shown above the π electrons are situated in the double bonds, shown in different positions in the two rings. The π electrons are not confined to any one position in the ring, so the

true benzene structure is an intermediate between the structures above. The benzene ring is considered a hybrid of these two structures and is not a mixture of two individual compounds. Like benzene, pyridine is described as a hybrid of resonating π electrons. But polar contributions are also present because of the presence of a nitrogen atom in the ring. The nitrogen attracts electrons from the 2 and 4 positions, using the numbering system



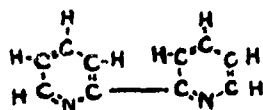
$$\begin{array}{ccccccc}
 \begin{array}{c} \text{H} \\ | \\ \text{H}-\text{C}_1-\text{C}_2-\text{C}_3-\text{H} \\ | \\ \text{H}-\text{C}_4-\text{N}-\text{C}_5-\text{H} \end{array} & \rightleftharpoons & \begin{array}{c} \text{H} \\ | \\ \text{H}-\text{C}_1-\text{C}_2=\text{C}_3-\text{H} \\ | \\ \text{H}-\text{C}_4=\text{N}=\text{C}_5-\text{H} \end{array} & \rightleftharpoons & \begin{array}{c} \text{H} \\ | \\ \text{H}-\text{C}_1-\text{C}_2=\text{C}_3-\text{H} \\ | \\ \text{H}-\text{C}_4=\text{N}^+-\text{C}_5-\text{H} \end{array} & \rightleftharpoons & \begin{array}{c} \text{H} \\ | \\ \text{H}-\text{C}_1-\text{C}_2^+-\text{C}_3-\text{H} \\ | \\ \text{H}-\text{C}_4=\text{N}^+-\text{C}_5-\text{H} \end{array} & \rightleftharpoons & \begin{array}{c} \text{H} \\ | \\ \text{H}-\text{C}_1-\text{C}_2=\text{C}_3-\text{H} \\ | \\ \text{H}-\text{C}_4=\text{N}^+-\text{C}_5-\text{H} \end{array} \\
 \underbrace{\hspace{10em}} & & & & \underbrace{\hspace{10em}} & & & & \\
 \text{Aromatic} & & & & \text{Polar contribution} & & & & \\
 \text{contribution} & & & & & & & &
 \end{array}$$

EXPERIMENTATION

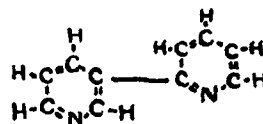
Materials. Pyridine: the Fisher Certified reagent was dried and distilled from calcium hydride, using a 50-plate bubble cap vacuum jacketed column (Bruun); the index of refraction was $n_D^{23.5^\circ\text{C}} = 1.5084$.

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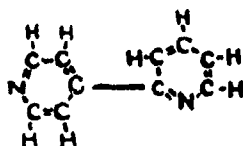
C. P. reagent. Other bipyridines were synthesized and purified as follows: 2,4'- and 4,4'- by the action of sodium upon pyridine(3); 2,3'- and 3,3'- from the corresponding phenanthrolines(4). Synthesis of 3,4'-bipyridine has not been accomplished yet, since a gas chromatography column has not been found to completely resolve the bipyridines. The respective structural formulae are:



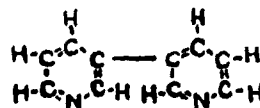
2,2'-Bipyridine



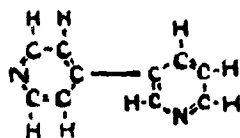
2,3'-Bipyridine



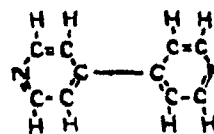
2,4'-Bipyridine



3,3'-Bipyridine



3,4'-Bipyridine



4,4'-Bipyridine

Calibration solutions for gas chromatograms: pyridine solutions of the five available bipyridines, 0.13 M in each bipyridine; both individual and composite solutions were prepared.

Irradiation. Exposures (about 50 hours) were made using a 120-curie Cs^{137} source (0.663-Mev gamma radiation). Dose rates were measured with the ferrous sulfate (Fricke) dosimeter using $G(\text{Fe}^{+++}) = 15.6$ (5); the value determined, 3.4×10^{20} electron volts/liter/hour or 5410 roentgens/hour, was corrected for the electron

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density of pyridine, becoming 4.9×10^{20} electron volts/liter/hour. Ferric concentrations were determined spectrophotometrically at 3040 Å.

Procedure. Using an all-glass high vacuum system, capable of 10^{-6} to 10^{-7} mm range Hg pressure, pure dry pyridine was degassed by a freeze-pump-thaw cycle repeated three times. To reduce contamination from vacuum stopcock grease, about 25 ml were distilled into a trap, thence to a second trap (a calibrated tube), and finally a measured volume was distilled into the irradiation cell, and the cell sealed off.

Following irradiation, the cell was attached to the vacuum line, opened, and the contents degassed as before. A Toepler pump was used to transfer the gaseous products thru two U-traps immersed first in dry-ice snow and then in liquid nitrogen. The non-condensable gas at each temperature was collected in the gas thimbles of the Blacet-Leighton apparatus.

The excess pyridine was distilled slowly into a reservoir. A small amount of pyridine was slowly distilled back to wash the residue down the walls, before the tube was cut off and the contents analyzed.

Analysis. Gas chromatography (or GC): non-gaseous radiolysis products were determined, in pyridine solution, on a Perkin-Elmer Vapor Fractometer Model 154 C. The 12-foot stainless steel column was packed with 0.25% Carbowax 1500 (polyethylene glycol) on glass beads (60/80 mesh). The column was maintained at $141 \pm 1^\circ\text{C}$, the flow rate of the helium carrier gas was 25.4 ml/min. This column gave much better resolution of bipyridines, than any other prepared. Even so, as noted below, the resolution was far from optimum and the retention times were extremely sensitive to temperature, solute concentration, and sample size.

Gas analysis: gaseous radiolysis products were analyzed on a Blacet-Leighton (Arthur H. Thomas Co. modification) micro gas analysis apparatus, according to the procedures described by Scott(6). Analysis were conducted for H_2 , C_2H_2 , C_2H_4 , CH_4 , and air (O_2 , and N_2 by difference).

Spectroscopy: ultraviolet absorption spectra of the non-gaseous radiolysis products were determined on a Cary Model 11 Recording Spectrophotometer, using 1 cm silica cells. IR spectra of these products were taken on a Perkin-Elmer Model 21 Double Beam Infrared Spectrophotometer equipped with a sodium chloride prism. Ferric ion concentrations were determined on a Beckman DUV Spectrophotometer using 1 cm silica cells.

RESULTS AND DISCUSSION

The major product of the irradiation of pyridine is about

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2 mg. of greenish yellow "varnish" and dark brown oily residue. The amount of gas formed was negligible. Small amounts (less than 150 mm³) of gas, non-condensable at liquid nitrogen temperatures, were collected in the thimbles. Upon analysis however, these samples proved to be air (20% O₂ + 80% inert gas, believed to be nitrogen) which may have been trapped in the Toepler pump outlet and carried out into the gas thimble.

A typical gas chromatography trace of the non-gaseous fraction is shown in Figure 1. Comparison of the traces with the calibration curve (Figure 2) identified the first peak as 2,2'-bipyridine. The second peak could not be identified as easily due to the lack of resolution for the remaining bipyridines.

Some interpretation of the GC traces is possible however. One does find a "clumping" of bipyridines in the calibration curve when compared to traces for the individual bipyridines. The retention times for the bipyridines, after normalization to the 2,2'-bipyridine peak as zero time are:

Bipyridine	Retention time, seconds corrected to 2,2'-bipyridine	Bipyridine boiling point, °C
2,3'-	795 ± 30	296
2,4'-	880 ± 33	297
3,3'-	1083 ± 47	301
4,4'-	1115 ± 30	305

The corresponding times for the second and third peaks of the calibration solution are 753 ± 53 and 936 ± 60 seconds. The lowering of retention times is due likely to the increased (5 times) solute concentration in the calibration solution as compared to the individual bipyridine solutions. The appearance of each isomer in the individual solutions was in order of its boiling point. Had 3,4'-bipyridine been present, it would have appeared later than the 2,4'-isomer(?) accordingly. We have assigned the peaks in the calibration solution as 753 seconds representing 2,3'- and 2,4'-bipyridine and 936 seconds the 3,3'- and 4,4'-compounds, after considering the respective boiling points and observed retention times.

The GC traces for the non-gaseous radiolysis product show a second peak at 665 seconds, normalized to the 2,2'-bipyridine peak. We believe this corresponds to the 753 second peak of the calibration curve. Although the concentration of solute was less than that of the calibration solution, the sample volume was two to threefold greater in order to put the largest amount of radiolysis product possible on the column. This larger sample volume may account for the reduced retention time.

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Further evidence for the presence of 2,2'- and one or both of 2,3'- and 2,4'-bipyridine in the residue is found in the ultraviolet absorption spectrum of the residue dissolved in 0.02 M NH₄OH(aq.) (Figure 3). Figure 4 shows the corresponding spectrum of equal amounts of 2,2'-, 2,3'-, 2,4'-, 3,3'-, and 4,4'- in 0.02 M NH₄OH(aq.) solution. Absorption maxima determined for the individual bipyridines(8), indicated on both figures, are:

Bipyridine	$\lambda, \text{\AA}$	$\lambda, \text{\AA}$
2,2'-	2800	2330
2,3'-	2750	2370
2,4'-	2730	2380
3,3'-	2690	2390
3,4'-	Inflection point at 2680	2410
4,4'-	Inflection point at 2700	2390

Differences in absorption or optical density are due to concentration differences. Most interesting is the position of the peak in the 2700-2800 Å region, which, for the solution of five bipyridines, appears midway (2730 Å) between the peaks given for the individual isomers. In Figure 3, the curve for the radiolysis product peaks at 2780 Å, midway between the 2,2'-, 2,3'-, and 2,4'- peaks. The bipyridines contributing to these peaks in Figure 3 must be among the 2,2'-, 2,3'-, and 2,4'-bipyridines. Infrared absorption spectra conducted on the pyridine solutions of the residue and on individual bipyridines did not resolve the identity of the residue further. Accordingly, the bipyridines are identified as the 2,2'- and 2,x'-isomers.

The yields of non-gaseous products were also determined from the GC calibration curve for the bipyridine solution. The amount of 2,2'-bipyridine was calculated from the peak area of the corresponding peak of the GC curve. The peak height of the 2,x'-bipyridine peak was correlated with the peak height of the 2,3'- + 2,4'-bipyridine peak on the calibration curve to determine the amount. Yields of product were determined as that formed per 100 electron volt energy input, and were calculated according to the formula

$$G = \frac{100 \times 6.02 \times 10^{23} \times M}{E \times V}$$

where G_{product} = yield of product/100 ev

M = moles product

E = irradiation dose, electron volts/liter

and V = volume of pyridine irradiated, liters

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The yields so calculated were:

$$G_{2,2'}\text{-bipyridine} = 0.11$$

$$G_{2,x'}\text{-bipyridine} = 0.20$$

$$G_{\text{bipyridine}} = 0.31$$

To determine if the results above represented the total non-gaseous radiolysis products, the weight of the product before GC analysis, was determined and compared with that calculated from the GC trace. Only about one-half the product is accounted for on the GC traces, so other compounds must be also present.

CONCLUSION

The gamma irradiation of liquid, oxygen-free and dried pyridine resulted in extremely low yields of product. By comparison, benzene, a chemical compound considered relatively stable to radiation, gave $G_{(H_2)} = 0.03$ and $G_{(\text{polymer})} = 0.98$ (1) (9). The gas yield from pyridine was undetectable by our methods. Had the H_2 yield been as large as that from benzene, about 7 mm³ would have been formed which would have been measurable.

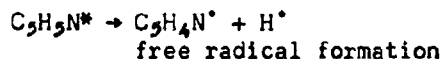
The polymer yield from benzene compares to our total bipyridine yield of 0.31 plus that of the non-gaseous products not yet identified. Hydrogenated dimer products ($C_{10}H_{10}N_2$, $C_{10}H_{12}N_2$, $C_{10}H_{14}N_2$, etc) and even trimers may be present. These dimer products would not differ greatly in molecular weight from the bipyridines ($C_{10}H_8N_2$), so that the yield (note weight measurements) should be somewhat similar. The asymmetry due to the N-atom of the pyridine ring, results in a great number of dimer (and trimer) isomers. The concentration of any one of these products would not likely be high enough to be detectable on the GC traces. Combustion analyses to determine C-H-N ratios, as well as molecular weight determinations, are necessary to clarify the remainder of the non-gaseous product. However, the $G(\text{pyridine} \rightarrow \text{polymer})$ according to our bipyridine and weight measurements would appear to be less than 1.

Aromatic compounds are characterized by low radiolysis yields, so that pyridine with total product yields no greater than that for benzene, shows aromatic behavior when irradiated. The nature of the non-gaseous product also conforms to the aromatic pattern, i.e. bipyridines compare to biphenyl (formed from benzene). A contribution from the polar nature of pyridine is found in the identity of the bipyridines formed (2,2'-; both or either of 2,3'-, 2,4'-). Quantum mechanical treatment of the pyridine resonance structure suggests the 2 position is most favored for radical attack and the 3 and 4 positions are next most favored equally (10). Further, though the type and total yields of product are comparable for pyridine and benzene, the distribution of products is different.

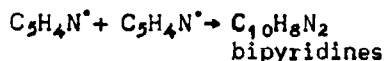
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With benzene $G(\text{biphenyl}) = 0.065$ (9) whereas for pyridine $G(\text{bipyridine}) = 0.31$. One infers that hydrogenated products are formed in much smaller amounts for pyridine.

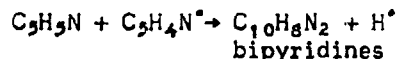
Consistent with the results, a radiolysis mechanism based upon the formation of free radicals has been formulated. This mechanism must account for the bipyridine formation, the absence of H_2 gas, and the formation of non-gaseous products so far unidentified, but perhaps hydrogenated isomers.



Radical recombination



may occur as well as reaction of the radicals with the solvent:



Interaction of $\text{H}^{\bullet}$ with other species present, i.e. $\text{C}_5\text{H}_5\text{N}$, $\text{C}_5\text{H}_4\text{N}^{\bullet}$, and $\text{C}_{10}\text{H}_8\text{N}_2$, could result in hydrogenated products, or in species which could react further to form such products. The recombination of $\text{H}^{\bullet}$ to form H_2 is not presented since the gas yield was undetectable. The formation of H_2 during benzene radiolysis is thought to come from non-radical processes(11), which would be consistent with our results and mechanisms.

Our results show pyridine reacts chiefly as an aromatic compound when irradiated. Important applications of this work may be possible in energy transfer media, in radiation protection, in biological studies, in reactor coolants, and in the creation of new radiation resistant materials.

ACKNOWLEDGMENT

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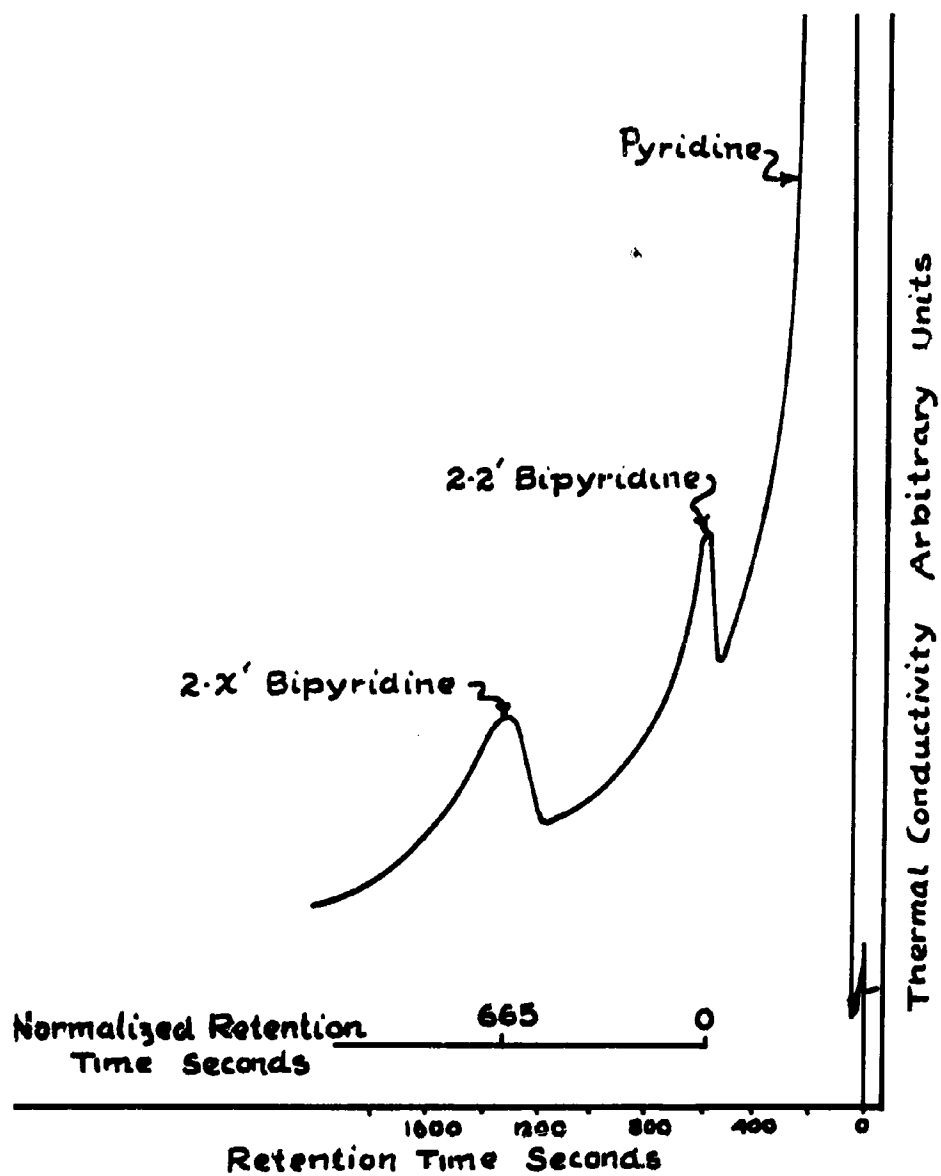


FIGURE 1
Gas Chromatogram of Non-Gaseous Products
from Irradiated Pyridine

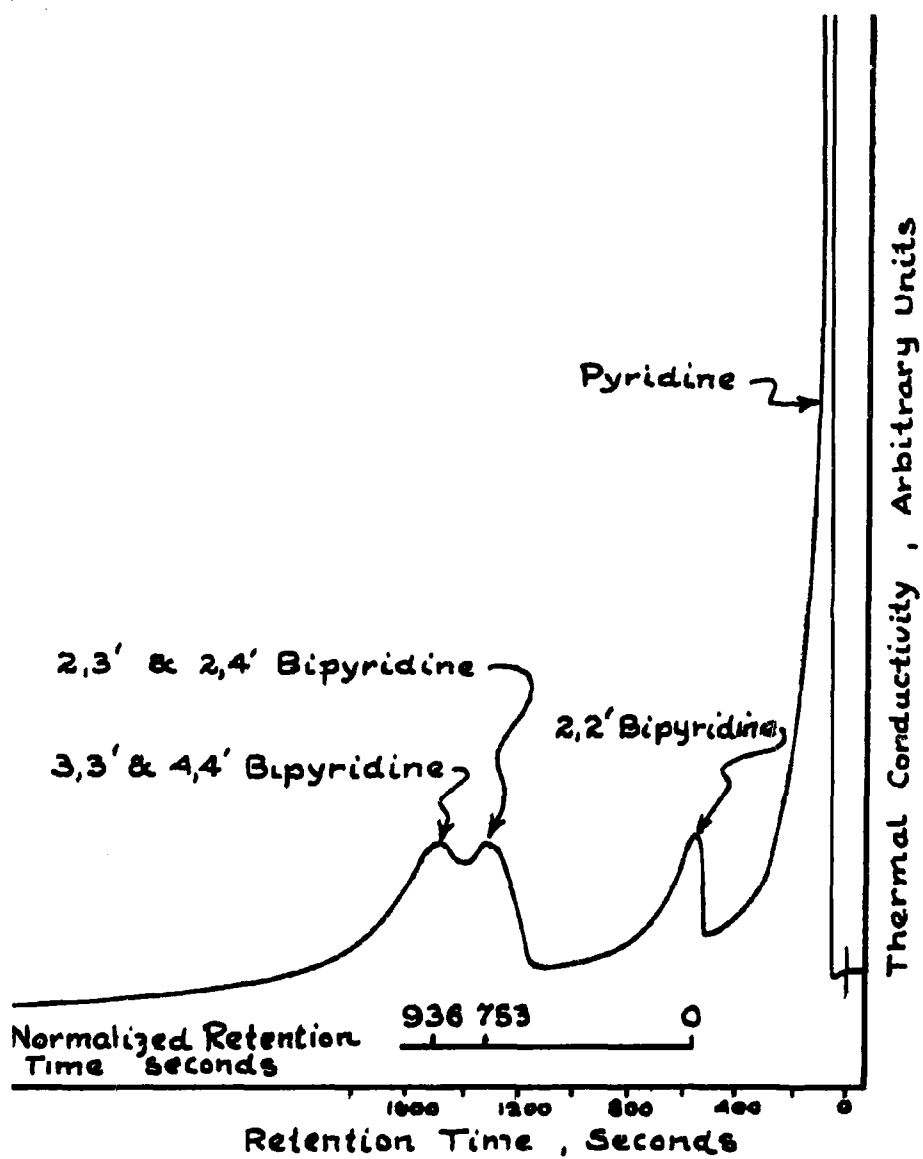


Figure 2
Gas Chromatogram of Bipyridine
Calibration Solution

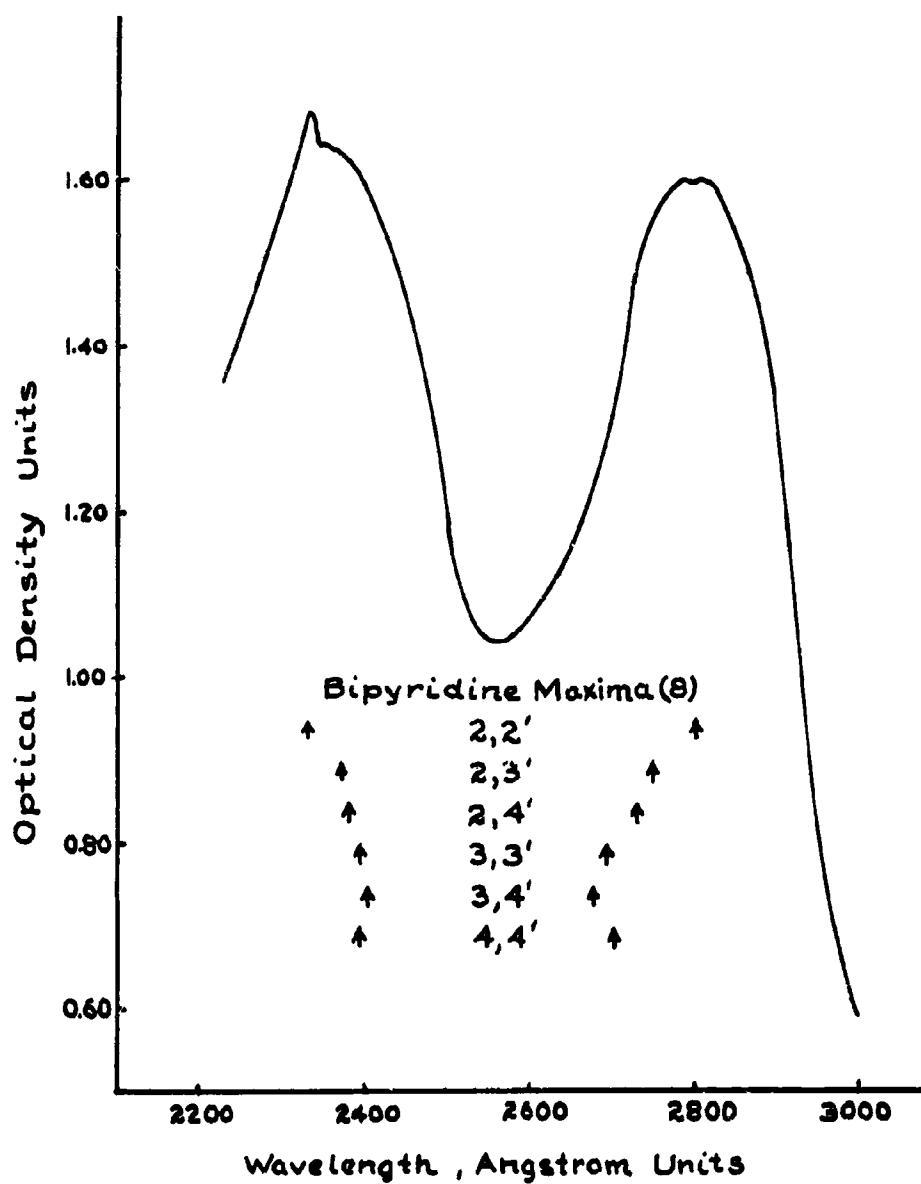


Figure 3
Ultraviolet Absorption Spectrum of Non-Gaseous
Products from Irradiated Pyridine

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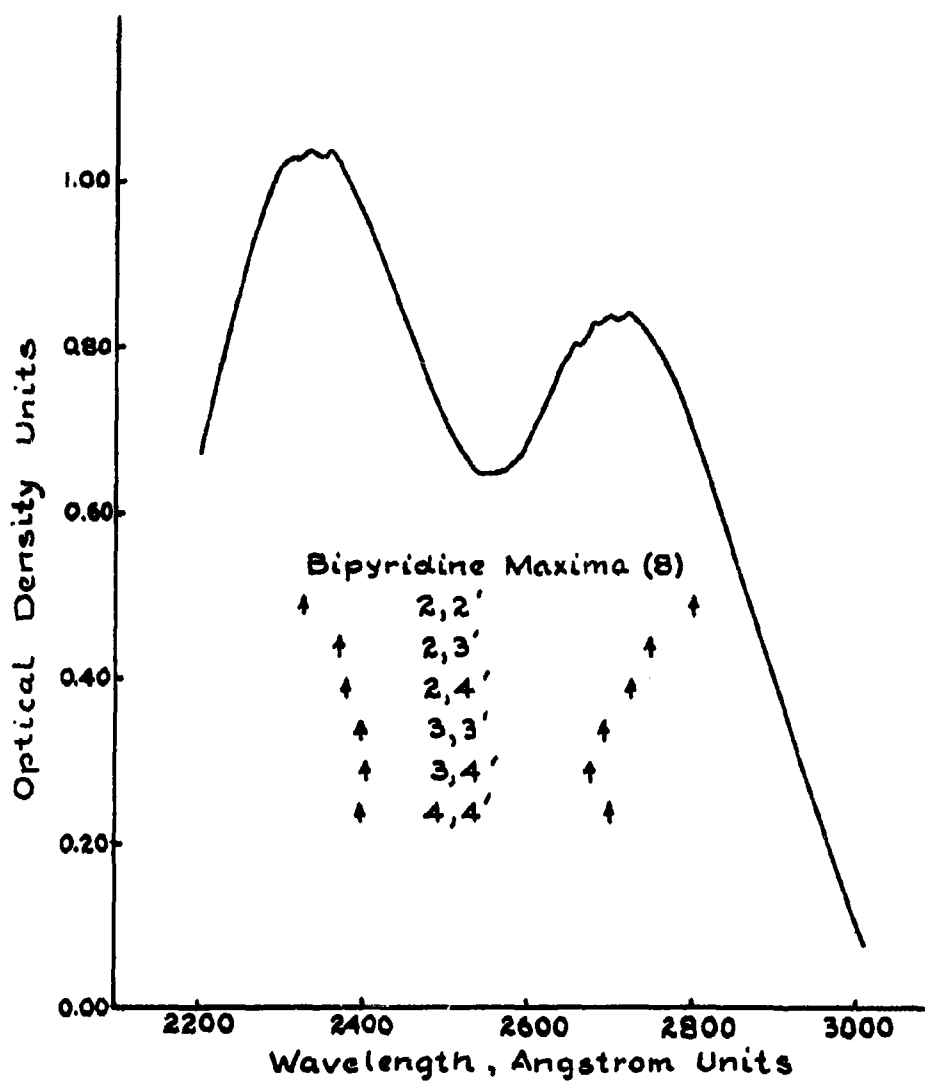


Figure 4

Ultraviolet Absorption Spectrum of Solution of
2,2' ; 2,3' ; 2,4' ; 3,3' ; 4,4' ; 3,4' ; Bipyridines

of free radicals is presented for the chemical effects of radiation on pyridine. (U)