The Fixation of Active Nitrogen By Organic Compounds

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The Fixation of Active Nitrogen by Organic Compounds

by F. Russell Koppa

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in Loyola University.

November, 1939.
The author was born in Chicago, Illinois on July 21, 1917. He was educated in the Chicago public schools, graduating from Carl Schurz High School in June, 1934. Wright Junior City College issued him a graduation diploma in June, 1936. In June, 1938 the College of Arts and Sciences of Loyola University bestowed the degree of Bachelor of Science upon him. From June, 1938 to the present he has been a graduate assistant of the Chemistry Department in the College of Arts and Sciences of Loyola University of Chicago.
The author gratefully acknowledges the competent assistance of Dr. Ardith P. Davis, who carefully supervised every step of the research and without whom the difficult task of constructing and assembling the apparatus could not have been done. Dr. Davis not only spent a great deal of time teaching the author the fundamentals of glass blowing, making valuable suggestions, and in observing the progress of the work, but he proved to be the inspiration of the work and a true friend of the author.

Acknowledgement is likewise made to each and every member of the Chemistry faculty for the numerous favors and assistance given to the author. Each in his own way has proved helpful.
The Fixation of Active Nitrogen
by Organic Compounds

Notwithstanding the widespread occurrence of nitrogen, few methods are known by which nitrogen can be made to combine directly with organic compounds. "Nitrogen is inert in the sense that it is difficult to initiate reactions in which free nitrogen takes part. It is usually necessary to raise the reacting components to a high temp. in order to inaugurate the reaction."¹ Mellor states that the chemical inertness of nitrogen is sometimes attributed to the relative stability of the molecules. When the molecule dissociates into atoms, $N_2 \leftrightarrow 2N$, it becomes very reactive. This is what happens when nitrogen is heated to high temperatures. Nitrides are thus formed with magnesium, aluminum, calcium, silicon, titanium, lithium, boron, zirconium, thorium, cerium, lanthanum, praseodymium, neodymium, samarium, chromium, tungsten, uranium, iron, and beryllium. Most nitrides furnish ammonia upon treatment with water.

In about 1861 A. Morren observed that a brilliant yellow luminescence was obtained by passing a condensed induction discharge through rarefied nitrogen. This luminescence persisted for a considerable time after cessation of the discharge. Similar observations were made by E. Sarasin (1876), E. Warburg (1884), E. Goldstein (1883), and E. P. Lewis (1900). Systematic investigation of this phenomenon was begun by R. J. Strutt (Lord Rayleigh) in 1910. Strutt demonstrated that many reactions which do not occur with ordinary nitrogen take place with the nitrogen gas in this condition. Nitrogen which has been exposed to an electric discharge is termed active or activated nitrogen.

Mellor\(^1\) states that "the duration of the after-glow is about 30 seconds. At first, the glow is orange-yellow, and slowly changes to greenish-yellow." Strutt showed that the intensity of the glow is increased by cooling the tube in liquid air although the glow disappears in the coldest part of the tube. If the tube through which the gas is passing be heated at one point the glow disappears, and the glow is permanently extinguished if the whole tube be strongly heated.

In the period between 1911 and 1915 considerable controversy and contradictions concerning the effect of im-

\(^{1}\)Ibid., p. 87.
purities in the nitrogen used occurred in the literature. Strutt and his followers (such as König and Elöd\(^1\)) on one side believed that the phenomenon was one concerned only with pure nitrogen. E. P. Lewis, F. Comte, and F. Tiede\(^2\) and others insisted that the phenomena of active nitrogen were not obtained in the absence of traces of oxygen.

Strutt has reviewed publications, some confirming the necessity of oxygen for the production of afterglow, others denying this.\(^3\) He states that "in the controversy which has been reviewed it was maintained, on the one side, that pure nitrogen would give the full effect, and, on the other, that the presence of oxygen was essential. It is now seen that, as in so many previous scientific controversies, neither side was entirely right. Almost any contamination, with the exception of argon and helium, increases the yield of active nitrogen, as judged by the intensity of the nitrogen afterglow....

"Perfectly pure nitrogen will not give more than a
little active nitrogen. On the other hand, to get a good yield it is not necessary that free oxygen or any oxygen compound should be present, for almost any small admixture of a foreign gas will enormously increase the yield of active nitrogen. The amount of admixture required to produce the best effect is usually of the order of 1/1000 part, but, to quote one case particularly examined, a very distinct effect is produced by adding a 1/30,000 part of methane."

On standing activated nitrogen gradually returns to normal nitrogen. This deactivation is rapidly accomplished in the presence of oxidized copper. The deactivation seems to be catalyzed by the walls of the vessel. The catalytic activity of the walls of the vessel can be reduced to a minimum by coating them with sulfuric acid or metaphosphoric acid. When the walls have been thusly treated the afterglow of active nitrogen has been visible for six or more hours.1


Lord Rayleigh in this publication states: "In present phase of work the question of minute impurities in nitrogen used is not considered....Quality of gas has been kept constant, and of a kind which is known to be satisfactory for the purpose. This is commercial cylinder nitrogen which has stood over moist phosphorus, and has been dried over
phosphorus pentoxide....The glass taps and joint were lubricated in the usual way with grease....Experience showed that there was no serious objection to the use of grease, which can only be avoided at the cost of considerable complication."

Kneser,¹ reviewing the reactions of activated nitrogen, states that it forms nitrides with the metals sodium, potassium, magnesium, calcium, zinc, cadmium, mercury, aluminum, thallium, tin, lead, and iron. Some of these nitrides have been identified chemically and some spectroscopically. With the exception of calcium and mercury the reactions occur only with the vaporized metals. Nitride formation occurs also with boron, arsenic, and sulfur. Unusual compounds frequently result. The product with sulfur is S₄N₄. With phosphorus a change resulting in the transformation of the white modification into the red occurs.

Up to the time of Kneser's publication Strutt² and Willey and Rideal³ were practically the only workers to

¹Kneser, Ergeb. exakt. Naturw., 8, 229 (1929).
active nitrogen with organic compounds and inorganic gases. These investigators showed that active nitrogen with a number of organic substances produced hydrogen cyanide. Among the organic substances producing hydrogen cyanide were benzene, pentane, heptane, methyl bromide, ethyl chloride, ethyl iodide, chloroform, bromoform, ethylene, ethylene dichloride, acetylene, and ethyl ether. The production of organic nitrogenous material was not demonstrated.

Howard and Hilbert¹ in 1938 published a series of experiments very similar to the one being reported. Theirs is to date the most carefully executed study of the fixation of active nitrogen by organic compounds. Diphenylacetylene, tetrahydronaphthalene, and benzonitrile were introduced into a reaction chamber with activated nitrogen. Howard and Hilbert reported that a "brown nitrogenous high-melting solid, hydrogen cyanide, excited cyanogen (CN*)..." resulted. "The brown solid, which is the major product of the reaction, appears to be a complex material of high molecular weight."

In their publication Howard and Hilbert stated that aromatic compounds were chosen for the research "since the aromatic portion of the molecule was expected to confer properties to the nitrogenated material which would make it
easy to handle....For comparative purposes, an exploratory experiment was performed to investigate the behavior of an aliphatic compound, isoprene, toward active nitrogen. A strikingly different result was secured. Practically no solid matter is formed and instead a nitrogenous low-boiling liquid in good yield and generating ammonia on hydrolysis is produced."

Strutt\(^1\) states that the intensity of the cyanogen glow accompanying the reactions differs from one compound to another and that perhaps the luminous effects are independent of the chemical ones. In all cases which he examined the glow was lilac colored in the absence of halogens.

It was intended in this investigation of the fixation of active nitrogen by organic compounds to determine whether nitrogen could be fixed by certain aliphatic compounds and, if so, to what extent the product resulting from active nitrogen differs from that when ordinary air is used in place of purified nitrogen.

It is hoped that a series of investigations of this problem will follow.
Apparatus and Experimental Procedure

The apparatus shown in Figure 1 was constructed. It consists principally of three parts: (1) a purification train for removing all but minute amounts of the oxygen and water from the nitrogen (2) a discharge tube for activating the nitrogen and (3) a reaction bulb with accessories for introducing the reactants and collecting the reaction products.

Ordinary compressed nitrogen was used in the experimental work. The suppliers state that the nitrogen "is of a purity of 99.5% or better with an oxygen content less than 0.5% by volume, and ordinarily the oxygen content is in the neighborhood of 0.2%, oxygen being the major impurity....As for any other impurities, there may be something like 0.0002% carbon dioxide and 0.00014% hydrocarbons present. In addition there may be an infinitesimal trace of inert gas...." The nitrogen from

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1 Letter of June 24, 1939 to author from A. N. Hanson, Puritan Compressed Gas Corp., Chicago.

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the tank was passed through the drying tower B, which contained concentrated sulfuric acid, and a tube C filled with potassium hydroxide pellets. The concentrated sulfuric acid was efficient in removing moisture from the gas
To pump J

G

N from nitrogen tank

Fig. 1. Apparatus for the fixation of active nitrogen by organic compounds.
as is evidenced by the fact that after eight months of experimental work the potassium hydroxide pellets in tube C show no evidence whatsoever of deliquescence. Tube C was 40 cm. long and 3 cm. in diameter. The gas passed from C through tube D, 4 cm. in diameter and 85 cm. long. Tube D was packed with copper turnings which had been oxidized with air and reduced with ordinary city gas; the tube was electrically heated at 450°. The gas was then cooled by trap F which was surrounded by a mush of solid carbon dioxide and acetone. After completion of the experiment the copper in tube D was easily regenerated by passing city gas through the tube by means of the three way stopcocks at either end. If the city gas were passed through the hot tube sufficiently quickly, steam was rapidly generated, and no difficulty was experienced in removing it from the apparatus. This operation was accomplished in a few minutes.

The discharge tube G utilized hollow aluminum\(^1\) electrodes, 2 cm. in diameter and 5 cm. long, which were mounted on tungsten leads. The current was produced by a General Electric sign transformer which was capable of delivering a secondary current of 30 milliamps at 15,000

volts. The path of the discharge between the electrodes was 1 meter long.

From G the activated nitrogen passed into the reaction bulb H where it encountered the organic vapors entering from the vaporizing chamber I. The resulting material collected in the trap J, cooled by the carbon dioxide-acetone mush. Trap J was fitted with a ground joint to facilitate removing the collected material and cleaning the trap after each sample. When necessary the organic material in I was vaporized by a water bath of the proper temperature.

The system A, consisting of two twelve liter flasks, was merely a device to maintain a constant pressure of nitrogen, since the nitrogen tank was not provided with a needle valve. The flasks were at all times partly filled with water.

A Megavac pump was used in the experimentation.

After preliminary experimentation with flowmeters a flowmeter of the type E was used. The longest arm of this flowmeter was about 100 cm. long. This flowmeter showed certain advantages over the ordinary type of flowmeter with arms 30-35 cm. long. Finer adjustments and readings were possible due to the large scale. No difficulty whatsoever was experienced in bringing the apparatus to atmospheric pressure after a sample had been collected. With
Fig. 2. Apparatus for calibration of flowmeter

From nitrogen tank
the ordinary type flowmeter the mercury from the arms frequently passed into other parts of the system unless extreme caution was exercised or traps were used in the upper arms of the flowmeter.

The apparatus devised and used for calibration of the flowmeter is shown in Figure 2. Vessel A is the water pop-off valve utilized in filling the vessel B with the nitrogen gas from the tank. A definite volume was drawn through the apparatus by the pump. This volume was measured by water levels passing markings on each side of vessel B. The leveling bulb C allowed the gas in B to be maintained at a constant pressure, i.e. atmospheric pressure. By noting the time required to pass the constant volume of nitrogen gas through the apparatus the rate of flow in c.c. per minute was calculated. At the same time readings were taken on the flowmeter scale. Flask B was of approximately one liter capacity. The drying tower D contained concentrated sulfuric acid to remove moisture vapor from the gas. The three way stopcock E was utilized in setting the approximately desired rate of flow with air and then quickly changing to the nitrogen gas. The stopcocks F merely served to facilitate settings of various rates of flow.

Approximately fifteen different rates of flow were determined. A curve was then constructed by plotting the difference in height of the mercury in the flowmeter arms
versus the rate of flow of nitrogen gas in c.c. per minute calculated to standard conditions. No difficulty was experienced in checking the curve. The following table gives the data for the calibration of the flowmeter.

Table for Calibration of Flowmeter

<table>
<thead>
<tr>
<th>Time</th>
<th>Flowmeter Readings</th>
<th>Calculated Rate of Flow at S.T.P. in c.c. per min.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Highest arm</td>
<td>Lowest arm</td>
</tr>
<tr>
<td>54.4&quot;</td>
<td>75.8 cm.</td>
<td>19.8 cm.</td>
</tr>
<tr>
<td>1' 00.2&quot;</td>
<td>73.3</td>
<td>22.2</td>
</tr>
<tr>
<td>1' 9.8&quot;</td>
<td>70.1</td>
<td>25.3</td>
</tr>
<tr>
<td>1' 17.0&quot;</td>
<td>68.3</td>
<td>27.1</td>
</tr>
<tr>
<td>1' 31.2&quot;</td>
<td>65.5</td>
<td>30.1</td>
</tr>
<tr>
<td>1' 43.9&quot;</td>
<td>63.6</td>
<td>31.9</td>
</tr>
<tr>
<td>1' 55.7&quot;</td>
<td>62.3</td>
<td>33.3</td>
</tr>
<tr>
<td>2' 14.1&quot;</td>
<td>60.5</td>
<td>35.1</td>
</tr>
<tr>
<td>3' 10.9&quot;</td>
<td>57.4</td>
<td>38.8</td>
</tr>
<tr>
<td>4' 23.4&quot;</td>
<td>55.3</td>
<td>40.4</td>
</tr>
<tr>
<td>5' 55.0&quot;</td>
<td>53.8</td>
<td>41.9</td>
</tr>
<tr>
<td>20' 35.3&quot;</td>
<td>50.5</td>
<td>45.3</td>
</tr>
</tbody>
</table>

Note: The time indicated in the table is the time measured with a stopwatch required for the water levels to pass the two markings on vessel B.

The accompanying graph gives the calibration curve for the flowmeter.

In the calibration of the flowmeter it would probab-
ly have been more satisfactory to have had D and E interchanged. Less fluctuations would then have resulted in changing from air to nitrogen gas since both gases would then have had to buck the pressure of the sulfuric acid in D.

In the calibration one observer recorded the time required for the water level to pass the markings on vessel B while another observer recorded the height of the mercury in each arm of the flowmeter.

After construction the apparatus was tested for leaks. The apparatus was evacuated to a pressure of 0.0002 mm. by means of a mercury vapor pump which had been sealed to the apparatus. The operation of the pump was discontinued, and the pressure changed only slightly over a period of five hours. A change in pressure would have indicated leakage at some point in the apparatus.

The procedure for carrying out the reactions were, in general, as follows: After the system had been adjusted with regards to pressure and rate of flow of nitrogen gas, the discharge tube was put into operation. A lemon-yellow afterglow then filled the reaction bulb. The intensity or brightness of the yellow color diminished with the distance from the discharge tube. It was observed that this yellow
color in the tube connecting the discharge tube and reaction flask did not reach its maximum intensity as soon as the discharge was put into operation. The intensity in color increased gradually until the maximum intensity of color was obtained in about one to two minutes. The water bath under I had been heated meanwhile to the proper temperature. As the temperature of the vessel rose and the organic material vaporized and entered the reaction bulb, a violet glow was noticeable for a short distance where the activated nitrogen entered the reaction bulb. When a large quantity of the organic material was allowed to enter the reaction flask in a relatively short time, i.e. when there was an excess of organic material in the reaction bulb, this violet glow was practically extinguished. If the pump and flow of nitrogen were discontinued this violet glow likewise filled the discharge tube. A series of samples were collected under varying conditions of rate of flow of nitrogen, pressure in apparatus, and quantity of organic material entering the reaction chamber. For each sample collected with nitrogen gas a corresponding sample was collected with air using approximately the same rate of flow of the two gases. In two cases (see accompanying table) when acetoacetic ester was used a brownish film
Table 2

Acetoacetic Ester Experimental Data

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Gas Used</th>
<th>Pressure in system in mm.</th>
<th>Rate of gas flow, c.c./min.</th>
<th>% Fixed Nitrogen</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Nitrogen</td>
<td>4.0</td>
<td>150</td>
<td>&lt;0.2%</td>
</tr>
<tr>
<td>2</td>
<td>Nitrogen</td>
<td>4.0</td>
<td>375</td>
<td>&lt;0.2%</td>
</tr>
<tr>
<td>3</td>
<td>Air</td>
<td>4.0</td>
<td>330</td>
<td>0.39, 0.53, 0.46</td>
</tr>
<tr>
<td>4</td>
<td>Nitrogen</td>
<td>5.5</td>
<td>475</td>
<td>0.26, 0.43, 0.35</td>
</tr>
<tr>
<td>Wall residue 4</td>
<td></td>
<td></td>
<td></td>
<td>1.89</td>
</tr>
<tr>
<td>5</td>
<td>Air</td>
<td>5.5</td>
<td>505</td>
<td>0.43, 0.47, 0.45</td>
</tr>
<tr>
<td>Wall residue 5</td>
<td></td>
<td></td>
<td></td>
<td>1.57</td>
</tr>
<tr>
<td>6</td>
<td>Nitrogen</td>
<td>7.5</td>
<td>670</td>
<td>0.55, 0.36, 0.46</td>
</tr>
<tr>
<td>7</td>
<td>Air</td>
<td>7.5</td>
<td>670</td>
<td>0.37, 0.54, 0.41</td>
</tr>
</tbody>
</table>

Note: In all cases the duration of the run was approximately 2½ hrs.

was observed on the walls of the reaction vessel opposite the point at which the activated gas entered.

In the experimental work with acetoacetic ester a twelve liter reaction flask was used. A large flask was originally chosen because the larger the vessel the greater is the ratio of volume to superficial area. This factor was at first thought to be important since, as stated before, deactivation of the active nitrogen is catalyzed by the walls of the vessel.
After all the sample had been collected, the discharge was discontinued and the pressure brought up to atmospheric pressure with the gas that had been used in the reaction. The carbon dioxide-acetone containers were removed. It was observed that a small quantity of moisture had condensed in trap F. With acetoacetic ester the color of the products in trap J varied from a colorless (the color of the pure acetoacetic ester itself) to a bright lemon yellow color. The greater part of the reaction product was liquid with the exception of the tarry brownish material mentioned above which collected in two cases on the walls of the reaction vessel.

The liquid material was removed from the trap J to a small container by means of a glass U-tube so operated that the transfer was accomplished without possible contamination of the product. The walls of the reaction vessel and the ground joint trap were then thoroughly cleaned by washing the vessels with first two portions of ether and then two portions of acetone. The cleaning of the reaction vessel was facilitated by the removal of the tightly fitting ground top. In the cases where the wall residue resulted this residue was separately collected by extraction of this residue with ether.

The samples were then subjected to the absolute nitrogen Dumas analysis. Eleven full days were spent in
preparing an apparatus which would generate nitrogen free carbon dioxide. Another difficulty encountered was the adsorption of air by the reagents in the combustion tube. However, when the directions in Fisher's laboratory manual


concerning combustions were observed, this difficulty was finally overcome.

In the cases of the ether extracts the larger part of the ether was removed from the viscous tarry material by evacuating the container to a pressure of c. 25 mm. for a period of approximately one hour. Merely to check the method and technique of analysis a sample of known composition was satisfactorily analyzed for nitrogen content.

Acetoacetic ester was originally chosen as a material for investigation because of the double bond in one tautomeric form which was expected to be vulnerable to the active nitrogen. The fact that the acetoacetic ester could be obtained easily, relatively cheaply, and of a high degree of purity was likewise important in its selection.

Cyclohexene was chosen as a second material for investigation. Primarily its unsaturated double bond was important. In this case the selection was made since there is only one possible structure, and no isomers of the substance are known. Likewise important is the fact that it
can be obtained easily, relatively cheaply, and of a high degree of purity.

While attempting to cleanse thoroughly the reaction flask after the acetoacetic ester work, the reaction flask was broken. Since this large flask was relatively expensive and its manipulation (especially the sealing of the three side arms to it) difficult, the flask was discarded and a one liter flask substituted for it. Since it was not desirous of unnecessarily complicating the apparatus, and yet it was necessary to be able to regulate the pressure of the apparatus during a determination, a capillary stopcock was sealed into the apparatus near the pump by means of which stopcock the pressure in the apparatus could be easily increased by slightly opening the stopcock to the air. Since the stopcock was quite far from the ground joint trap and the pump was in full operation when the stopcock was opened, there was no possibility of air in any way affecting the collected product.

With the one liter. flask in the apparatus pulsation of the lemon yellow glow in the arm connecting the discharge tube and reaction bulb was observed. This pulsation was sympathetic with the strokes of the Megavac pump. This pulsation was not observed in the work with acetoacetic ester when the twelve liter reaction flask was used.

The cyclohexene used was the best obtainable having
a boiling point range of 82--84°. Its relatively low boiling point necessitated cooling the vaporizing chamber in an ice bath while the apparatus was in operation. It was thus fairly difficult to regulate the rate of flow of cyclohexene into the reaction bulb.

Cyclohexene imparted a beautiful deep violet glow to the discharge tube when the pump and flow of gas into the apparatus was discontinued.

The experimentation was performed in a manner similar to the experimentation with acetoacetic ester. However after the reaction product had been collected in the ground joint trap, it was transferred to a 50 ml. distilling flask (care being taken to prevent contamination of the product by transferring with a U-tube using suction to draw the liquid from one vessel into the other). The unreacted cyclohexene was then distilled from the resulting product. All material beneath the boiling point range of cyclohexene, 82--84°, was discarded. The product then remaining was combined with the ether extract of any wall residue resulting from the wash portions of the ether used to cleanse the reaction flask walls.

After evaporation of the ether from this extract the resulting product was subjected to the Dumas nitrogen analysis. In some cases chloroform was also used as a solvent for the dark colored viscous material which resulted,
since chloroform seemed to have very slightly better solvent properties for this material than did ether.

About half of the product obtained from these reactions in all cases was dissolved in the cyclohexene condensed in the trap. The insoluble part collected in the form of a drop, or in some cases as droplets, at the bottom of the cyclohexene. This indicated that its density was greater than 0.8102, the density of cyclohexene. In all cases the product was colored, varying from a pale yellow to a deep brown. The darker material was generally very viscous and resinous.

The slight solubility of the material in the original cyclohexene indicates a material of greatly different structure from the cyclohexene or, more probably, a polymerized reaction product.

Table 3 summarizes the data on the experimentation with cyclohexene.

It should be noted that these figures do not give the total yield of fixed nitrogen. In each case a relatively thin film of residue remained in the trap and reaction chamber. This was not readily soluble in the common solvents, and it was thus impossible to analyze this material by the Dumas method without considerable difficulty.
Table 3
Cyclohexene Experimental Data

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Gas Used</th>
<th>Length of run</th>
<th>Pressure in system</th>
<th>Rate of gas flow, c.c./min.</th>
<th>% Fixed Nitrogen</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>Nitrogen</td>
<td>1 hr.</td>
<td>7 mm.</td>
<td>350</td>
<td>2.10%</td>
</tr>
<tr>
<td>21</td>
<td>Air</td>
<td>1½ hr.</td>
<td>7.2</td>
<td>350</td>
<td>6.30</td>
</tr>
<tr>
<td>22</td>
<td>Nitrogen</td>
<td>½ hr.</td>
<td>8.2</td>
<td>643</td>
<td>4.39</td>
</tr>
<tr>
<td>23</td>
<td>Air</td>
<td>1½ hr.</td>
<td>7.3</td>
<td>630</td>
<td>3.15</td>
</tr>
</tbody>
</table>

Discussion and Conclusions

From the results indicated in Table 2 it is concluded that active nitrogen reacts with acetoacetic ester to yield a product containing less than 2% of fixed nitrogen. The product was amber to pale brown in color. This product seemed to be a complex mixture.

Cyclohexene reacts with active nitrogen to yield a product containing between 2.0 and 6.5% nitrogen. This product was resinous in nature, less soluble in the common solvents than was the product in the case of acetoacetic ester, and it was amber to deep brown in color.

Only a relatively small amount of the nitrogen passed through the discharge tube was fixed.

The products resulting from similar treatments with
purified nitrogen and air are different as indicated by the different percentages of fixed nitrogen and the color of the products. The author wishes to point out here that Howard and Hilbert¹ state "That nitrogen oxides are not involved to any great extent...." in the reactions which they studied. Howard and Hilbert's observation regarding the purity of the nitrogen and its effect on the persistence of the discharge with pressure was checked. It was observed that as the oxygen content of the gas was diminished the greater was the pressure at which the discharge persisted.

Color changes indicate that the greatest amount of polymerization and fixation of nitrogen occur while the viscous, oily, solid-like material is further bombarded with active nitrogen while still remaining on the walls of the vessel.

The reaction product in the case of cyclohexene appears to be more markedly different from the original material than does the product resulting from acetoacetic ester.

¹Howard and Hilbert, Op. cit., p. 1922
Bibliography


The thesis, "The Fixation of Active Nitrogen by Organic Compounds", written by F. Russell Koppa, has been accepted by the Graduate School with reference to form, and by the readers whose names appear below, with reference to content. It is, therefore, accepted in partial fulfillment of the requirements for the degree of Master of Science.

Ardith P. Davis, Ph.D. November 8, 1939
George M. Schmeing, Ph.D. November 15, 1939
Joseph D. Parent, Ph.D. December 1, 1939