THE HETEROGENEOUS DECOMPOSITION OF HYDRAZINE:
PART 2, THE USE OF N\textsubscript{2} AS A TRACER TO STUDY THE DECOMPOSITION OF HYDRAZINE ON THE SHELL 465 CATALYST
by
C. F. Sayer

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THE HETEROGENEOUS DECOMPOSITION OF HYDRAZINE: PART 2,
THE USE OF N₁⁵ AS A TRACER TO STUDY THE DECOMPOSITION OF HYDRAZINE
ON THE SHELL 405 CATALYST

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SUMMARY

The origin of nitrogen produced by catalytic decomposition of liquid hydrazine has been studied by measuring the distribution of N₁⁵ in nitrogen produced from N₁⁵-enriched hydrazine in a large excess of normal hydrazine. From isotope abundance ratios deduced from mass spectrometric analysis it appears that hydrazine decomposes on the Shell 405 catalyst (iridium on alumina) to give nitrogen in which both atoms come from the same hydrazine molecule. The overall reaction may be represented by

$$3 \text{N}_2\text{H}_4 \rightarrow \text{N}_2 + \frac{3}{2} \text{NH}_3$$

side reactions producing a little hydrogen. Hydrazine hydrochloride decomposes on the same catalyst, without side reactions, in exact accordance with

$$3 \text{N}_2\text{H}_5^+ \rightarrow \text{N}_2 + \frac{3}{2} \text{NH}_3 + 3 \text{H}^+$$

also without N-N bond fission.

Using rhodium as the catalyst, both hydrazine and hydrazine hydrochloride decompose to give nitrogen molecules, the two atoms of which stem from the same hydrazine molecule, according to the reactions

$$2 \text{N}_2\text{H}_4 \rightarrow \text{N}_2 + \text{H}_2 + 2 \text{NH}_3$$

$$2 \text{N}_2\text{H}_5^+ \rightarrow \text{N}_2 + \text{H}_2 + 2 \text{NH}_3 + 2 \text{H}^+$$
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INTRODUCTION

The kinetics of the liquid phase decomposition of hydrazine on a supported iridium catalyst (the Shell 405 catalyst) have been studied recently and the reaction was found to be first-order with respect to hydrazine concentration over the range 15-100% w/w hydrazine. The activation energy for the reaction was calculated to be 15,628 ± 22 cal mole⁻¹. The gas chromatographic analysis of the gaseous products of the decomposition indicated that no hydrogen was produced and the reaction was represented by

\[
3 \text{N}_2\text{H}_4 \rightarrow \text{N}_2 + 4 \text{NH}_3
\]

Other workers² have considered the platinum metals, with the exception of osmium, for the decomposition of hydrazine and from their work there is an indication that the gaseous products may be different using a rhodium catalyst.

This report describes the use of N₁⁵ as a tracer to study the formation of nitrogen gas produced by the decomposition of hydrazine on iridium and rhodium catalysts. In addition, the decomposition of hydrazine hydrochloride has also been studied. The products of the decomposition of hydrazine on rhodium and iridium catalyst have been analysed and the results are presented.

EXPERIMENTAL

2.1 Materials

The sample of hydrazine rich in N₁⁵ was obtained from Isotopes Incorporated, Westwood, New Jersey, USA, as an aqueous solution, the nitrogen isotope content being 96.2 atom percent N₁⁵ and 3.8 atom percent N₁⁴. The N₁⁵ - enriched hydrazine was diluted with propellent grade hydrazine, 97.7% w/w (Olin Mathieson Corporation), and made up to 25 ml in a volumetric flask with distilled water. The concentration of the stock solution was 30.8% w/w hydrazine. The weights of hydrazine used, as confirmed by mass spectrometric analysis of nitrogen gas from the stock solution, were 0.119 gm N₁⁵ - enriched and 7.776 gm propellent grade hydrazine; the molar dilution ratio was 1 mole of enriched hydrazine to 65.3 moles propellent grade.
hydrazine. For a second hydrazine concentration 1.858 gm stock solution was added to 0.502 gm propellent grade hydrazine to give a solution of 45% w/w hydrazine concentration in which the dilution ratio was 1 mole enriched hydrazine to 122.3 moles propellent grade hydrazine.

The iridium catalyst consisted of 33% iridium on an alumina support (Shell 405 catalyst obtained from the Shell Development Company, USA) in the form of 1/8 inch dia pellets. The rhodium catalyst, also in the form of 1/8 inch pellets, consisted of 20% rhodium on an alumina support, obtained from Engelhard Industries Limited, Cinderford, Gloucestershire.

2.2 Product analysis

The apparatus used in conjunction with the gas chromatograph is shown in Fig. 1. The apparatus was purged with argon, until analysis showed that all the air had been removed. Argon was also used as the carrier gas in the gas chromatograph. The catalyst was dropped into the hydrazine solution by rotation of the side-arm and the gaseous products sampled by means of the chromatograph sampling valve. The gas chromatograph column was packed with Linde Molecular Sieve Type 5A and was calibrated with hydrogen and nitrogen obtained from cylinders of compressed gas.

The apparatus shown in Fig. 2 was used to determine the number of molecules of ammonia produced by the decomposition of each molecule of hydrazine. A solution of about 20% w/w hydrazine was prepared and the concentration determined by titration with 0.25M potassium iodate solution in hydrochloric acid solution using carbon tetrachloride as an adsorption indicator ("Andrews" titration). The total alkali concentration (hydrazine plus ammonia) was determined by titration with 0.5N hydrochloric acid solution using methyl orange indicator. The difference between the two titrations, in moles, represents any ammonia present in the hydrazine solution.

An aliquot of the standardized hydrazine solution was placed in the flask and 50 ml 0.1N hydrochloric acid placed in the receiver flask. The catalyst pellets
were then dropped into the hydrazine solution and a slow current of air pumped through the apparatus to sweep any gaseous ammonia through the acid receiver flask. After a reasonable quantity of hydrazine had been decomposed the hydrazine solution was transferred to a 250 ml volumetric flask, the reaction flask and the catalyst pellets were well washed with distilled water and the washings added to the volumetric flask before the solution was made up to 250 ml with distilled water. Separate 25 ml aliquots of the hydrazine solution were then titrated with 0.5N hydrochloric acid and 0.25M potassium iodate, and the 0.1N hydrochloric acid in the receiver flask was titrated with 0.1N sodium hydroxide to determine the amount of ammonia absorbed. The standardization of the hydrazine solution by "Andrews" titration gave the starting concentration of hydrazine and the "Andrews" titration at the end of an experiment gave the finishing concentration. The difference between these two figures was the amount of hydrazine decomposed. Ammonia present in the starting material (25 ml aliquot) was equivalent to 0.15 ml 0.5N hydrochloric acid and the acid titration at the finish was corrected by this amount. The total alkali content (hydrazine plus ammonia) was given by the corrected titre plus the moles of acid used in the acid receiver flask, the amount of ammonia produced being the difference between the total alkali content and the moles hydrazine found by "Andrews" titration after reaction.

2.3 The use of $^{15}N$ as a tracer

The apparatus used for the preparation of nitrogen gas samples from the decomposition of hydrazine is shown in Fig. 3. A lower reaction vessel containing the hydrazine solution had a B14 socket in the side wall into which fitted the catalyst holder. The gas sample bottles were of 100 ml capacity, and the reaction vessel and gas bottles fitted onto a T-piece which connected them to the vacuum pump and a mercury manometer.

Sufficient hydrazine solution to produce, on decomposition, a nitrogen pressure in the system greater than one atmosphere was placed in the reaction vessel and the solution frozen in liquid nitrogen. The system was evacuated by pumping and then
isolated from the vacuum pump and checked for leaks. When the system was proved to be free from leaks the hydrazine was allowed to melt and the reaction vessel immersed in water at 70°C to boil out air from the hydrazine solution. The solution was then refrozen in liquid nitrogen and the whole procedure repeated a further four times. The hydrazine solution was then allowed to reach room temperature and the catalyst pellets dropped into the solution by rotating the catalyst holder through 180°. The pressure in the system was monitored by means of the manometer and when the pressure reached 780 mm Hg absolute the gas sample bottle was sealed and the reaction stopped by immersing the solution in liquid nitrogen. The pressure in the system was taken above atmospheric so that any gas leakage through the gas sample bottle stopcock would be to the atmosphere. The gas was then analysed for the three nitrogen mass numbers, 28, 29 and 30, and also for oxygen on a Metropolitan-Vickers Type MS2 mass spectrometer.

3 RESULTS

3.1 Product analysis

The results of the analysis of the gaseous products of decomposition, by gas chromatography, are given in Table 1. The results are for hydrogen and nitrogen; no ammonia analysis was carried out at this stage, as some of the ammonia would dissolve in the hydrazine solution and give a low value for the ammonia content. For the decomposition of hydrazine on an iridium catalyst (Shell 405) the average hydrogen to nitrogen molar ratio is 1 to 166; for the decomposition of hydrazine hydrochloride on the iridium catalyst no hydrogen could be detected. For the rhodium catalyst the decomposition of both hydrazine and hydrazine hydrochloride result in a hydrogen to nitrogen molar ratio of 1 to 1.

In Table 2 are given the results of the "Andrews" and acid titrations to determine the number of molecules of ammonia formed from the decomposition of each molecule of hydrazine. For the iridium catalyst each molecule of hydrazine decomposed produced 1.33 molecules of ammonia, whilst with the rhodium catalyst one molecule of ammonia was produced for each molecule of hydrazine decomposed.
3.2 The use of $^{15}N$ as a tracer

The figures given in Table 3 are the calculated nitrogen gas isotope abundance ratios based on the molar dilution ratio of $^{15}N$ enriched hydrazine to propellant grade hydrazine and the total atom percent of $^{15}N$. Values are calculated for mechanisms that involve 0, 50 and 100% of N-N bond fission of original hydrazine molecules. These figures are discussed later.

The isotope abundance ratios given in Table 4 are the results of the mass spectrometric analyses of the nitrogen gas samples from the decomposition of hydrazine. The results for the 30.8% stock solution, in the form of hydrazine or hydrazine hydrochloride, on both the iridium and rhodium catalyst agree well with the calculated results for no N-N bond fission in forming nitrogen. This result is confirmed by the experiment with the 45% stock solution and the Shell 405 catalyst. The use of ceric sulphate to oxidise a sample of 30.8% hydrazine in acid solution produced nitrogen in which approximately 50% of the N-N bonds had been broken.

4 DISCUSSION

The product analysis was carried out to determine which overall reactions may be used to represent the decomposition of hydrazine on the iridium and rhodium catalysts. Possible ones are

\begin{align*}
3 \text{N}_2\text{H}_4 & \rightarrow \text{N}_2 + 4 \text{NH}_3, \\
3 \text{N}_2\text{H}_4 & \rightarrow 2 \text{N}_2 + 2 \text{NH}_3 + 3 \text{H}_2, \\
2 \text{N}_2\text{H}_4 & \rightarrow \text{N}_2 + 2 \text{NH}_3 + \text{H}_2, \\
\text{N}_2\text{H}_4 & \rightarrow \text{N}_2 + 2 \text{H}_2.
\end{align*}

The gas chromatographic analysis was carried out to determine the nitrogen to hydrogen ratio. A separate analysis for ammonia and hydrazine was carried out using titrimetric techniques.
From the results in Table 2 the decomposition of hydrazine on the iridium catalyst yields 1.33 molecules of ammonia for each molecule of hydrazine decomposed; this result agrees with the hydrazine to ammonia ratio of 1.33 in reaction (1) above. However, by gas chromatography (Table 1) the permanent gas produced by the decomposition of hydrazine on the iridium catalyst contained approximately 0.6% hydrogen. This small amount of hydrogen is presumably produced by one, or more, of the other reactions represented above. When the iridium catalyst was used to decompose hydrazine hydrochloride the gas chromatographic analysis of the permanent gas produced gave 100% nitrogen and no hydrogen was detected. Hence by analogy with reaction (1), used to represent the decomposition of hydrazine, the decomposition of hydrazine hydrochloride on the iridium catalyst may be represented by

\[ 3 \text{N}_2\text{H}_5^+ \rightarrow \text{N}_2 + 4 \text{NH}_3 + 3 \text{H}^+ \] (5)

For the decomposition of hydrazine on the rhodium catalyst the molar conversion ratio of hydrazine into ammonia given in Table 2 is 1 to 1, and in Table 1 the molar ratio of hydrogen to nitrogen is also 1 to 1. These results agree with the ratios in reaction (3) above and the decomposition of hydrazine on the rhodium catalyst may therefore be represented by

\[ 2 \text{N}_2\text{H}_4 \rightarrow \text{N}_2 + \text{H}_2 + 2 \text{NH}_3 \] (3)

In Table 1 the decomposition of hydrazine hydrochloride on the rhodium catalyst results in a hydrogen to nitrogen ratio of 1 to 1, and hence, by analogy with the reaction used to represent the decomposition of hydrazine on the rhodium catalyst,

\[ 2 \text{N}_2\text{H}_5^+ \rightarrow \text{N}_2 + \text{H}_2 + 2 \text{NH}_3 + 2 \text{H}^+ \] (6)

may be used.

The decomposition of hydrazine yields nitrogen as one of the gaseous products and the formation of nitrogen under these conditions has been studied using \(\text{N}^{15}\) as a tracer. The isotope abundance ratios given in Table 3 are the results which have
been calculated based on the atom percent $N^{15}$ and the molar dilution ratios used to prepare the stock solution and the following assumptions concerning the formation of nitrogen.

The original sample of $N^{15}$-enriched hydrazine contains 96.2 atom percent $N^{15}$ and 3.8 atom percent $N^{14}$, and assuming the nitrogen atoms are distributed in the statistical proportions according to the expression

$$\left[ \frac{N^{15}H_2}{N^{14}H_2} \right]^2 \left/ \left[ \frac{(N^{15}_2H_4)}{(N^{14}_2H_4)} \right] \right. = 4 \quad , \quad (7)$$

then the mole percent distribution of the isotopically different forms of hydrazine is

$$\begin{align*}
n^{15}N_2H_4 & \quad N^{15}H_2 \quad N^{14}H_2 \quad N^{14}_2H_4 \\
92.55\% & \quad 7.31\% \quad 0.14\% \quad .
\end{align*}$$

For normal hydrazine the $N^{15}$ content may be assumed to be 0.38 atom percent, the same as for nitrogen in the atmosphere $^4$, and the statistical proportions in this case give the distribution

$$\begin{align*}
n^{15}N_2H_4 & \quad N^{15}H_2 \quad N^{14}H_2 \quad N^{14}_2H_4 \\
0.00144\% & \quad 0.757\% \quad 99.2\% \quad .
\end{align*}$$

To prepare the stock solution of hydrazine of 30.8% w/w concentration, $N^{15}$ enriched hydrazine was diluted with normal hydrazine in the molar dilution ratio of 1 mole $N^{15}$ enriched hydrazine to 65.3 moles normal hydrazine. The calculated distribution for the stock solution is

$$\begin{align*}
n^{15}N_2H_4 & \quad N^{15}H_2 \quad N^{14}H_2 \quad N^{14}_2H_4 \\
1.396\% & \quad 0.856\% \quad 97.73\% \quad .
\end{align*}$$
The calculated $^{15}N$ content of the stock solution is 1.824 atom percent.

From the calculated distribution for the isotopically different forms of hydrazine in the stock solution and the $^{15}N$ content it is possible to calculate the isotope abundance ratios given in Table 3 making assumptions as to the possible mechanisms for the formation of nitrogen from hydrazine.

If the decomposition of hydrazine follows a mechanism in which the nitrogen atoms of a hydrazine molecule remain bonded together throughout the reaction sequence then the nitrogen formed will have the same isotope distribution as that of the stock hydrazine solution, namely

$$\begin{align*}
N_2^{30} & \quad N_2^{29} & \quad N_2^{28} \\
1.396\% & \quad 0.856\% & \quad 97.73\%
\end{align*}$$

and the isotope abundance ratios derived from these values are given in Table 3 for the stock solution of 30.8% hydrazine.

If, on the other hand, all the N-N bonds in the hydrazine molecules are broken in the decomposition then the nitrogen will be formed by the recombination of nitrogen-containing fragments. This recombination process may be assumed to be a purely random process and the isotope distribution of the nitrogen so formed may be calculated according to the statistical expression given above (equation (7)) from the calculated $^{15}N$ content of 1.824 atom per cent. The calculated statistical isotope distribution is

$$\begin{align*}
N_2^{30} & \quad N_2^{29} & \quad N_2^{28} \\
0.033\% & \quad 3.581\% & \quad 96.4\%
\end{align*}$$

The isotope abundance ratios calculated from these values are given in Table 3 for 100% N-N bond fission for 30.8% hydrazine solution.

These are the two extreme mechanisms for the formation of nitrogen produced by the decomposition of hydrazine. A third mechanism is now considered. This
mechanism has been postulated\(^5\) to account for the formation of nitrogen consisting of half the molecules having both nitrogen atoms from one hydrazine molecule and half having the two nitrogen atoms from different hydrazine molecules. This mechanism was found to operate for the oxidation of hydrazine in acid solution by such oxidizers as ceric sulphate. In the initial steps \(N_2H_3\) radicals are formed which dimerize and then break down

\[
N_2H_3 + H_2 \rightarrow N_4H_6 \rightarrow NH_3 + NH = N - NH_2 , \tag{8}
\]

\[
NH = N - NH_2 \rightarrow H_2 + NH_3 . \tag{9}
\]

If the nitrogen atoms are labelled by \(N^{15}\) then the following reaction scheme may be written to account for partial randomization. Using the superscripts 'a' and 'b' to identify the hydrazine molecule from which the nitrogen atoms originate

\[
N^aH_2 + N^bH_2 \rightarrow H_2[N^a-N^bH_2] \rightarrow H_2N^a-N^bH_2 \rightarrow \ (N^a = N^b - N^bH_2) \tag{10}
\]

\[
H_2N^a - N^bH_3 \rightarrow N^a = N^b - N^bH_2 \rightarrow N^b + N^bH_3 , \text{ etc.}
\]

Such a mechanism results in 50\% \(N-N\) bond fission and the calculated isotope abundance ratios are given in Table 3.

A second stock solution of hydrazine was prepared from 1.858 gm of the 30.8\% stock solution further diluted with 0.502 gm of propellant grade hydrazine. The concentration of the resulting solution was 45\% hydrazine and the molar dilution ratio was 1 mole \(N^{15}\) enriched hydrazine to 122.3 moles propellant grade hydrazine; the calculated \(N^{15}\) content of the solution was 1.157 atom percent. The isotope abundance ratios calculated on the basis of the three mechanisms outlined above are given in Table 3.
The results of the mass spectrometric analyses carried out on the nitrogen gas samples are given in Table 4. Both stock solutions of hydrazine were decomposed on the iridium catalyst and the resulting isotope abundance ratios for the nitrogen samples agree closely with the calculated results based on the assumption that no N-N bond fission occurs in the formation of nitrogen. The decomposition of the 30.8% stock hydrazine solution on the rhodium catalyst also resulted in nitrogen gas samples having isotope abundance ratios close to those predicted for no N-N bond fission. In this example the $N^{15}$ content is 5% higher than the calculated value and as the isotope abundance ratios indicate only 3% N-N bond fission, within the experimental error of the analysis no bond fission is indicated. The results of decomposition of hydrazine hydrochloride on both the iridium and rhodium catalysts also indicate that N-N bond fission does not occur.

As all the results of the decomposition of hydrazine on the catalysts showed that no N-N bond fission occurred, it was decided to carry out experiments on a reaction known to proceed through a mechanism involving some N-N bond fission to show that the randomization could be detected. The reaction chosen was the oxidization of hydrazine in acid solution by ceric sulphate. The same apparatus was used, the catalyst holder contained the ceric sulphate in the form of a fine powder and after the hydrazine solution had been degassed the oxidizer was added to the solution and the nitrogen sample taken in the usual way. The result of the mass spectrometric analysis is shown in Table 4 and the isotope abundance ratios are in reasonable agreement with the values calculated on the basis of 50% N-N bond fission shown in Table 3. The result of approximately 50% randomization is in good agreement with the results of Higginson and Sutton, who found that the percent randomization varied slightly according to the equivalents of oxidizing agent used for each mole of hydrazine.

**CONCLUSIONS**

The decomposition of hydrazine on an iridium catalyst yields mainly nitrogen and ammonia together with a small amount of hydrogen. The main reaction for the
decomposition of hydrazine may be represented by

$$3 \text{N}_2\text{H}_4 \rightarrow \text{N}_2 + 4 \text{NH}_3$$

and side reactions occur to produce traces of hydrogen. The nitrogen molecules are derived from the decomposition of the hydrazine without any N-N bond fission.

Similarly the decomposition of hydrazine hydrochloride on the iridium catalyst may be represented by

$$3 \text{N}_2\text{H}_5^+ \rightarrow \text{N}_2 + 4 \text{NH}_3 + 3 \text{H}^+$$

In this reaction no hydrogen gas is produced. The nitrogen molecules are derived from the decomposition of the hydrazine hydrochloride without any N-N bond fission.

Likewise, N-N bond fission does not occur during the formation of nitrogen in the decomposition of hydrazine on a rhodium catalyst. However, hydrogen is formed as a major product and the reaction may be represented by

$$2 \text{N}_2\text{H}_4 \rightarrow \text{N}_2 + 2 \text{NH}_3 + \text{H}_2$$

Similarly, the decomposition of hydrazine hydrochloride on a rhodium catalyst may be represented by

$$2 \text{N}_2\text{H}_5^+ \rightarrow \text{N}_2 + \text{H}_2 + 2 \text{NH}_3 + 2 \text{H}^+$$

and again no N-N bond fission occurs in the formation of the nitrogen.

Acknowledgements

The author wishes to acknowledge the assistance of Mr. J. R. McLean with the gas chromatographic analysis. The author also wishes to thank Dr. A. R. Hall for providing time on the MS2 mass spectrometer and Mr. A. C. I'Anson who carried out the mass spectrometric analyses.
TABLE 1
Gas chromatographic analysis of the gaseous products of decomposition

<table>
<thead>
<tr>
<th>Hydrazine sample/catalyst</th>
<th>Gas analysis</th>
<th>Molar ratio</th>
<th>H₂ : N₂</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>H₂</td>
<td>N₂</td>
<td></td>
</tr>
<tr>
<td>20% N₂H₄/iridium</td>
<td>0.4</td>
<td>99.6</td>
<td>1</td>
</tr>
<tr>
<td>50% N₂H₄/iridium</td>
<td>1.0</td>
<td>99.0</td>
<td>1</td>
</tr>
<tr>
<td>95% N₂H₄/iridium</td>
<td>0.5</td>
<td>99.5</td>
<td>1</td>
</tr>
<tr>
<td>N₂H₅Cl/iridium</td>
<td>-</td>
<td>100</td>
<td>-</td>
</tr>
<tr>
<td>20% N₂H₄/rhodium</td>
<td>50.6</td>
<td>49.4</td>
<td>1</td>
</tr>
<tr>
<td>50% N₂H₄/rhodium</td>
<td>50.5</td>
<td>49.5</td>
<td>1</td>
</tr>
<tr>
<td>95% N₂H₄/rhodium</td>
<td>51.8</td>
<td>48.2</td>
<td>1</td>
</tr>
<tr>
<td>N₂H₅Cl/rhodium</td>
<td>50.6</td>
<td>49.4</td>
<td>1</td>
</tr>
</tbody>
</table>

TABLE 2
Determination of the molar conversion of hydrazine to ammonia
in the decomposition of hydrazine

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Moles of hydrazine</th>
<th>Total moles alkali</th>
<th>moles NH₃ produced</th>
<th>N₂H₄ : NH₃ ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Start¹</td>
<td>Finish²</td>
<td>Change³</td>
<td></td>
</tr>
<tr>
<td>Iridium</td>
<td>0.0232</td>
<td>0.0092</td>
<td>0.0140</td>
<td>0.0278</td>
</tr>
<tr>
<td></td>
<td>0.0232</td>
<td>0.0126</td>
<td>0.0106</td>
<td>0.0269</td>
</tr>
<tr>
<td></td>
<td>0.0232</td>
<td>0.0091</td>
<td>0.0141</td>
<td>0.0279</td>
</tr>
<tr>
<td></td>
<td>0.0232</td>
<td>0.0092</td>
<td>0.0140</td>
<td>0.0278</td>
</tr>
<tr>
<td>Rhodium</td>
<td>0.0232</td>
<td>0.0226</td>
<td>0.0006</td>
<td>0.0232</td>
</tr>
<tr>
<td></td>
<td>0.0232</td>
<td>0.0194</td>
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</tr>
<tr>
<td></td>
<td>0.0232</td>
<td>0.0074</td>
<td>0.0153</td>
<td>0.0228</td>
</tr>
<tr>
<td></td>
<td>0.0232</td>
<td>0.0056</td>
<td>0.0176</td>
<td>0.0235</td>
</tr>
</tbody>
</table>

Notes:
1 Moles of hydrazine determined by Andrews titration.
2 Moles of hydrazine remaining after reaction, determined by Andrews titration.
3 Moles of hydrazine decomposed, given by (1-2).
4 Total alkali (hydrazine and ammonia) after reaction, determined by acid titration plus moles of acid used in the acid receiver flask.
5 Moles of ammonia produced given by (4-2).
### TABLE 3

**Calculated nitrogen gas isotope abundance ratios for the stock solutions of hydrazine**

<table>
<thead>
<tr>
<th>Hydrazine solution</th>
<th>Amount of N-N bond fission, per cent</th>
<th>Isotope abundance ratios</th>
<th>per cent $^{15}N$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>28/30</td>
<td>28/29</td>
<td>28/30</td>
</tr>
<tr>
<td>30.8%</td>
<td>0</td>
<td>0.613</td>
<td>114.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>70.0</td>
</tr>
<tr>
<td>30.8%</td>
<td>50</td>
<td>3.1</td>
<td>43.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>135.8</td>
</tr>
<tr>
<td>30.8%</td>
<td>100</td>
<td>108.0</td>
<td>27.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2930</td>
</tr>
<tr>
<td>45.0%</td>
<td>0</td>
<td>1.08</td>
<td>122.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>130.0</td>
</tr>
<tr>
<td>45.0%</td>
<td>50</td>
<td>4.05</td>
<td>63.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>256.0</td>
</tr>
<tr>
<td>45.0%</td>
<td>100</td>
<td>176.1</td>
<td>42.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>7515</td>
</tr>
</tbody>
</table>

### TABLE 4

**Mass spectrometry results for nitrogen gas analysis**

<table>
<thead>
<tr>
<th>Hydrazine solution/ catalyst</th>
<th>Isotope abundance ratios</th>
<th>per cent $^{15}N$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>28/30</td>
<td>28/29</td>
</tr>
<tr>
<td>30.8% $N_2H_4$/iridium</td>
<td>0.615 ± 0.005</td>
<td>112.0 ± 2.0</td>
</tr>
<tr>
<td>$N_2HCl$/iridium</td>
<td>0.655 ± 0.015</td>
<td>110.5 ± 2.5</td>
</tr>
<tr>
<td>30.8% $N_2H_4$/rhodium</td>
<td>0.71 ± 0.05</td>
<td>98.25 ± 5.25</td>
</tr>
<tr>
<td>$N_2HCl$/rhodium</td>
<td>0.675 ± 0.025</td>
<td>101.25 ± 1.25</td>
</tr>
<tr>
<td>45.0% $N_2H_4$/iridium</td>
<td>1.06 ± 0.02</td>
<td>125.5 ± 3.5</td>
</tr>
<tr>
<td>$N_2I_4$/Ir* oxidiser</td>
<td>2.95 ± 0.05</td>
<td>44.1 ± 3.3</td>
</tr>
<tr>
<td>No.</td>
<td>Author</td>
<td>Title, etc.</td>
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<td>4</td>
<td>A. L. Vaughan, J. H. Williams, J. T. Tate</td>
<td>Isotope abundance ratios of C, N, A, Ne and Ne. Phys. Review, 46, 327 (1934)</td>
</tr>
</tbody>
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ATTACHED:—

Drugs. RP 4906, 4907
Detachtable abstract cards
FIG. 1 APPARATUS FOR CHROMATOGRAPHIC ANALYSIS OF GASEOUS PRODUCTS OF DECOMPOSITION

FIG. 2 APPARATUS FOR DETERMINING MOLAR CONVERSION OF HYDRAZINE TO AMMONIA IN THE DECOMPOSITION OF HYDRAZINE
FIG. 3 APPARATUS FOR PREPARATION OF NITROGEN GAS SAMPLES