Summer 1961

THE RADIATION INDUCED EXCHANGE OF CARBON BETWEEN ETHANE AND METHYL AMINE

PHILIP SHEPARD LAMPREY
University of New Hampshire, Durham

Follow this and additional works at: https://scholars.unh.edu/dissertation

Recommended Citation
https://scholars.unh.edu/dissertation/2366

This Dissertation is brought to you for free and open access by the Student Scholarship at University of New Hampshire Scholars' Repository. It has been accepted for inclusion in Doctoral Dissertations by an authorized administrator of University of New Hampshire Scholars' Repository. For more information, please contact nicole.hentz@unh.edu.
THE RADIATION INDUCED EXCHANGE OF CARBON BETWEEN ETHANE AND METHYL AMINE

Keywords
Chemistry, Physical

This dissertation is available at University of New Hampshire Scholars' Repository: https://scholars.unh.edu/dissertation/2366
THE RADIATION INDUCED EXCHANGE OF CARBON BETWEEN
ETHANE AND METHYL AMINE

BY
PHILIP SHEPARD LAMPREY
B.S., Lowell Technological Institute, 1956

A THESIS
Submitted to the University of New Hampshire
In Partial Fulfillment of
The Requirements for the Degree of
Doctor of Philosophy

Graduate School
Department of Chemistry
July, 1960
ACKNOWLEDGMENT

The author wishes to express his thanks to the University of New Hampshire Chemistry Department and its chairman, Dr. Harold Iddles, for aid and encouragement in this work.

In particular, the author expresses his sincere gratitude to Dr. Alexander Amell under whose direction this work was done. It was Dr. Amell who made this work possible under an Atomic Energy Commission research grant. His unfailing optimism in times of deepest doubt was truly inspirational; his assistance and thoughtfulness will long be remembered.

Philip S. Lamprey
# LIST OF TABLES

<table>
<thead>
<tr>
<th>NUMBER</th>
<th>TABLE DESCRIPTION</th>
<th>PAGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Analysis of Brookhaven Sample A</td>
<td>39</td>
</tr>
<tr>
<td>2.</td>
<td>Series 1 Data: Effect of Varying Irradiation Time Upon Exchange</td>
<td>40</td>
</tr>
<tr>
<td>3.</td>
<td>Series 2 Data: Effect of Varying Methyl Amine Content Upon Exchange</td>
<td>41</td>
</tr>
<tr>
<td>4.</td>
<td>Series 3 Data: Effect of Varying Ethane Content Upon Exchange</td>
<td>43</td>
</tr>
<tr>
<td>5.</td>
<td>Exchange Results</td>
<td>44</td>
</tr>
<tr>
<td>6.</td>
<td>Series 4 Data: Gas Chromatographic Analysis</td>
<td>46</td>
</tr>
</tbody>
</table>
### LIST OF ILLUSTRATIONS (Continued)

<table>
<thead>
<tr>
<th>NUMBER</th>
<th>Illustration Description</th>
<th>PAGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>16.</td>
<td>Plot of Specific Activity as a Function of Methyl Amine Concentration</td>
<td>50</td>
</tr>
<tr>
<td>17.</td>
<td>Plot of Total Activity as a Function of Ethane Concentration</td>
<td>51</td>
</tr>
<tr>
<td>18.</td>
<td>Plot of Specific Activity as a Function of Ethane Concentration</td>
<td>52</td>
</tr>
<tr>
<td>19.</td>
<td>Plot of Total Activity as a Function of (ml.-cm. of Ethane)$^3$</td>
<td>53</td>
</tr>
<tr>
<td>20.</td>
<td>Plot of Exchange &quot;G&quot; Value as a Function of Ethane Concentration</td>
<td>54</td>
</tr>
<tr>
<td>21.</td>
<td>Sample 4-D Gas Fractometer Curve</td>
<td>55</td>
</tr>
<tr>
<td>22.</td>
<td>Sample 4-D Ionization Chamber Curve</td>
<td>56</td>
</tr>
</tbody>
</table>
the recoil due to antineutrino emission, and the angular correlation of the beta particle and the antineutrino. These two factors are difficult to determine and at best only rough approximations of their effect have been attempted\(^3\).

In spite of the complexity of the theoretical considerations, it is evident that recoil imparted by beta emission has a definite probability of rupturing chemical bonds. A limited number of studies of this phenomena have been carried out\(^4\), the most elaborate being the work of Wolfgang, Anderson, and Dodson using double labelled carbon-14 ethane\(^5\). If one of the carbon-14 atoms in double labelled ethane undergoes beta decay and the recoil does not break the C-N bond, the product should be \((\ce{C^{14}H_3NH_3+})\), which is assumed to give \(\ce{C^{14}H_3NH_2}\), labelled methyl amine. On the other hand, if the carbon-nitrogen bond is ruptured due to the beta decay, labelled methyl amine will not be the product. Thus, by determination of labelled methyl amine which has "grown into" a sample of doubly labelled ethane, the number of beta decays in which the C-N bond is not ruptured can be calculated.

Wolfsberg has treated the decay of doubly labelled carbon-14 ethane from a theoretical standpoint\(^6\). He considers not only the recoil effect in bond rupture, but also the effect of change of atomic number accompanying beta decay on the rupture possibility. The beta decay of carbon-14 of atomic number six results in a product of nitrogen-14 with an atomic number of seven. This change of atomic number
However, it might be possible that an effect considered as negligible by Wolfgang, Anderson, and Dodson is significant. This is the effect of self irradiation of the sample. Carbon-14 decays by emitting a beta particle of 0.155 million electron volts maximum energy. It is possible that these beta particles in passing through the samples produce a radiation effect that could affect the results of bond rupture studies.

One radiation effect would be induced exchange of carbon atoms. The species present in the samples studied by Wolfgang et al. were doubly labelled ethane, singly labelled ethane, and non-labelled ethane. The overall result of a radiation induced exchange is shown in (2). In this equation C* and C represent different isotopes of carbon.

\[
\text{CH}_2\text{NH}_2 + \text{C*H}_3 - \text{C*H}_3 \xrightarrow{\text{beta}} \text{C*H}_3 - \text{NH}_2 + \text{CH}_3 + \text{C*H}_3 \quad (2)
\]

or

\[
\text{C*H}_3 - \text{CH}_3
\]

If the amount of recoil rupture of bonding is studied by activity analysis of methyl amine, it is evident that the radiation induced exchange would affect the results.

Another radiation effect that could possibly mask bond rupture study in this system is radiation decomposition of methyl amine. Such a decomposition of methyl amine into \( \text{CH}_3 \) and \( \text{NH}_2 \) fragments is shown in (3). The products, of course, must react further to become stable molecules.

\[
\text{CH}_3 - \text{NH}_2 \xrightarrow{\text{beta}} \text{CH}_3 + \text{NH}_2 \quad (3)
\]
The possibility of radiation decomposition is supported by the plots in figure 1, which have been made up from the data of Wolfgang et al. These show an apparent relationship between grow-in time (i.e., time of self irradiation) and experimentally determined bond retention. This could be interpreted as a radiation decomposition of the methyl amine. As the methyl amine concentration builds up, the probability of radiation acting upon it increases. The result of this decomposition would be to lower the values found experimentally for bond retention. Such appears to be the case for the data plotted in figure 1; however, more data is necessary to substantiate the decrease in retention with grow-in time.

Wolfgang et al, eliminate the possibility of radiation induced exchange on the basis of one sample which had carrier methyl amine present during the grow-in period. They report that the added carrier had no significant effect on the bond retention results. Amell, however, has found that added methyl amine carrier increases apparent bond retention to values greater than 100%.

The main intent of the work described in this thesis is to determine whether or not there is a radiation induced exchange of carbon between ethane and methyl amine, and if there is an exchange, the effects of varying radiation dose, pressure of methyl amine, and pressure of ethane.

Carbon-14 has a half life of 5570 years. Because of this long half life it takes an inconveniently long time to
grow in a measurable amount of methyl amine and to produce a significant amount of internal radiation. For this reason it was decided to study radiation induced exchange in this system by introducing large doses of radiation in a relatively short time, and by introducing inactive methyl amine before the irradiations. The large dose of radiation in a short time is made possible by use of a cobalt-60 source which is described elsewhere in this thesis.
BOND RETENTION AS A FUNCTION OF GROW-IN TIME

This data is taken from the work of Wolfgang, Anderson, and Dodson.

. A Samples
+ B Samples
x C Samples

FIGURE 1

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.
APPARATUS AND PROCEDURES

1. Apparatus.

A. Cobalt-60 Irradiation Source.

The construction of the cobalt irradiator, with the exception of pouring of lead for a shield, was carried out in this laboratory. The shield was poured by Laboratory Associates Inc. of Belmont, Massachusetts. The irradiator was designed by Dr. Alexander Amell.

A diagram of the cobalt-60 irradiator is shown in figure 2. The irradiator is kept in a small isolated radiation building on the University campus.

The shield (Fig. 3A) consists of 600 pounds of lead in a cylindrical steel casing. A one inch square center hole allows control of the source. A section is cut out so that the sample insert can be placed in the shield.

The source itself consists of 150 curies (June, 1958) of cobalt-60 in the form of wafers which are contained in a brass capsule 2 1/2 in x 3/4 in. x 3/4 in. The capsule is attached by a screw thread to a vertical metal rod, which is in turn connected by means of a laboratory type screw clamp to a horizontal metal rod (source positioning rod) which extends over the concrete wall. This wall is five feet high and two feet thick. All manipulation of the source is done from behind it. The source positioning rod has another rod connected perpendicular to it at the end behind
of the sample insert. The source fits into the center area of these vessels as shown in 4-A. The smaller vessels (4-B) were used for all gas phase irradiations. One to six of these can be taped to the inside of a tin can which is then placed on the insert platform.

Actual introduction of the samples to the source is done by a novel yet efficient method. In order to introduce a sample vessel, the source must be raised by means of the source control rod, locked in the raised position, and the sample insert moved out of the shield. An 8 foot piece of laboratory rubber tubing, with an ordinary balloon, wired on the end, is threaded through a ring attached to the end of a 6 foot metal rod. The balloon is then placed inside the sample vessel, inflated, and the tubing pinched to keep it so. The vessel is then swung over the wall and the metal bar is manipulated until the vessel goes through the insert holding ring and onto the sample platform. A mirror is hung over the source and so adjusted that the sample container can be watched from behind the wall during the introduction procedure. The balloon is then allowed to deflate and is removed from the container, following which the insert is closed, and the source moved to the down position. Sample containers are removed from the irradiator by reversing this procedure.

On June 19, 1958, the encapsulated cobalt-60 source, purchased from Oak Ridge National Laboratories was transferred to the irradiator.
A.H. Thomas Company, was employed for combustion of methyl phenyl thiourea derivatives to carbon dioxide.

A special glass connecting line, similar to that described by Van Slyke, Steele, and Plazin, was prepared in order that the carbon dioxide from the combustion apparatus could be transferred to counting tubes for activity determinations.

D. Counting Tubes and Scaler.

The counting tubes used were similar to those described by Bernstein and Ballentine. These tubes afford easy counting of gas phase low energy beta emitters in the proportional region. The fractional active volumes of the tubes were determined as suggested by Bernstein and Ballentine. Tube 3 gave a value of 0.86, and tube 4 gave a value of 0.854.

The tubes were used in conjunction with a Nuclear-Chicago Model 186 decade scaler. A special cylindrical lead shield was used to accommodate the counting tubes. Using this shield, the background count of tube 3 was 4986 counts/hour and that of tube 4 was 5366 counts/hour.

E. Gas Chromatograph and Ionization Detector.

Initially gas chromatographic work was done on a chromatograph prepared in this laboratory by D. Shonting. After the desired separations appeared to be feasible, a Perkin Elmer Model 154 Vapor Fractometer was obtained. Column packings were prepared in this laboratory. In preliminary work a General Electric chart recorder (Model #8CE5CF7A) was connected to the Fractometer; however, in runs employing
the ionization chamber, described below, a Sargent Model SR recorder was connected to the Fractometer and the General Electric recorder was used with the ionization chamber.

The gas sampling device of the Fractometer was altered somewhat for this work (see figure 7). Two metal female ball joints were threaded at the end in order to fit into the Fractometer sampling valve. A pyrex sampling vessel was designed that would fit these joints and could also be employed on the vacuum line to freeze out samples to be chromatographed. This vessel, when used on the vacuum line, was held so that the coil loop could be placed in liquid nitrogen. Two three way stopcocks were used in this vessel in order to have the Fractometer come to equilibrium with the carrier gas flow bypassing the sample and in order to be able to quickly switch the sample chamber into the carrier gas flow.

A flow type ionization chamber, shown in figure 8, was designed to be used in conjunction with the Fractometer to study the products of irradiation of carbon-14 ethane, methyl amine mixtures. The ionization chamber was used with an Applied Physics Corporation Model 30 vibrating reed electrometer. In use, the chamber, which is made of brass and has a volume of about 15 milliliters, was connected to the Fractometer outlet by a short piece of rubber tubing. A polarizing potential of 9 volts was supplied by dry cells.

* This instrument was kindly loaned to us by Dr. John Lockwood of the U.N.H. Physics Department.
IRRADIATION VESSELS

FIGURE 4

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.
A. VACUUM LINE

A,B,C,D,E,F,G,H are vacuum stopcocks
I is a 3 way stopcock
M,N are ground joints
J,K,L are gas storage vessels
N is a side arm trap

B. DERIVATIVE PREPARATION APPARATUS

FIGURE 6
CHROMATOGRAPHIC SAMPLING VESSEL

FIGURE 7

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.
2. Procedures

1. Preparation of Chromatographic Columns.

The various chromatographic columns tested for separation of the amines were prepared as follows:

Either Johns Manville C-22 ground firebrick or Johns Manville Celite 545 was sieved, the 40-60 mesh portions being retained. This material was then heated in a muffle furnace for three hours at 300°C, and washed with concentrated HCl to remove iron and basic impurities. After being washed to remove the acid, the material was oven dried at 145°C. Before use the material was treated with 5% (W/V) methanolic NaOH, decanted, and oven dried at 100°C. It was then stored in a dessicator over solid NaOH. The particular liquid phase to be studied was added to the material in the ratio of 3 grams of liquid phase to 7 grams of solid, and the two were mixed. The prepared packing was packed into glass chromatographic columns using a Burgess Vibratool to promote evenness. In the laboratory made chromatograph, the column consisted of a straight glass tubing of 10 mm i.d. and 2.4 meters length. In the Vapor Fractometer, the column consisted of two glass U shaped tubes of 4 mm i.d. and each of 1 meter length.

The prepared column was put into the instrument being used and the carrier gas (helium) allowed to flow for a period of 1-2 hours in order for the detecting device (a thermal conductivity cell for the laboratory made chromatograph and a thermistor circuit for the Vapor Fractometer)
and the pressure of ethane in the burette measured. From this pressure and the calibrated volume of the burette, previously determined by weighing displaced mercury, the amount of ethane present could be determined. Ethane was allowed to leak into the vacuum line by slightly opening stopcock C until only the desired amount remained in the burette. C was then closed, a Dewar of liquid nitrogen placed at L, stopcock G opened, and the excess ethane allowed to freeze back into L. In 5-10 minutes G was closed, the liquid nitrogen Dewar removed from L and placed at the sample vessel connected at M. The stopcock to the sample vessel was then opened as was stopcock C, allowing the measured ethane sample to freeze into the vessel. Stopcock E, connecting methyl amine containing storage bulb, L, to the line was slightly opened, then closed. A Dewar of liquid nitrogen was then placed at the burette side arm with stopcock open. After 5-10 minutes C was closed, the liquid nitrogen bath removed, the methyl amine allowed to vaporize, and the pressure and volume measured. Methyl amine above the desired amount for the particular sample was allowed to leak back into the line and was frozen into bulb J as the excess ethane was allowed to return to bulb L, and the measured amount of methyl amine was transferred to the sample vessel in the same manner as the ethane. The burette stopcock, C, was then closed as was the sample vessel stopcock. The sample vessel was then sealed off under vacuum while its end was in a Dewar of liquid nitrogen.
The glass sample vessels were taped inside small cardboard cylinders in order to protect the break seal. Up to six of these cylinders were taped around the inside of a can, which could then be introduced into the irradiator.

B. Sample Analysis and Specific Activity Determinations.

The long grow-in time samples, prepared at Brookhaven laboratories, were handled in the same manner as the irradiated samples, the only difference being that the Brookhaven samples were in one liter flasks, whereas the irradiated samples were in the vessels previously described. The Brookhaven samples were run first as the ethane recovered from them was used in the irradiation work.

The Brookhaven one liter vessels were attached to the vacuum line by a male ground joint attached through a break seal. The irradiation vessels were attached to the line, inside a glass tube of 14 mm i.d. and about 35 cm. in length, which had been sealed off at one end. A glass en-cased nail was placed in this tube and it was sealed to a male ground joint. For both the liter flasks and the irradiation vessels, the ground joint fit female joint, M, of the vacuum line.

The actual procedure for sample analysis, which is similar to that described by Wolfgang, Anderson, and Dodson⁵, was as follows:

The sample vessel was connected to the line which was then pumped to about $10^{-4}$ mm of mercury pressure. Stopcock A was then closed and the vessel break seal broken. A Dewar
of liquid nitrogen was placed at the gas burette side arm and stopcock C opened. In 5-10 minutes C was closed, the liquid nitrogen removed, the sample allowed to vaporize, and its pressure and volume measured and recorded. The flask of liquid nitrogen was then placed around the freezing coil (O) of the vacuum line and stopcock C was opened. In 5-10 minutes the Dewar of liquid nitrogen was transferred to the burette side arm and was quickly replaced at the coil by a Dewar containing melting isopentane. Stopcock C was then opened. Under this differential of cooling baths (isopentane: -160°C, nitrogen: -196°C) the ethane distilled to the gas burette and the methyl amine remained in the freezing coil.* In 10-15 minutes stopcock C was closed, the liquid nitrogen removed, the ethane allowed to vaporize and its pressure and volume recorded. In order to transfer the ethane from the burette to its storage bulb, the liquid nitrogen Dewar was placed at the storage bulb, L, and stopcock G opened. In 5-10 minutes G was closed and the liquid nitrogen removed. A small amount of inactive ethane was allowed to enter the vacuum line from its storage bulb, K, by quickly opening and closing stopcock F. The melting isopentane was removed from the coil and replaced by the Dewar of liquid nitrogen. In 5-10 minutes the liquid nitrogen bath was removed, replaced by melting isopentane, the nitrogen placed at bulb K, and stopcock F opened. In 5-10 minutes F was closed and the liquid nitrogen

* One of the Brookhaven samples (A) contained no carrier methyl amine, so that previous to this step an amount of carrier methyl amine was added to the sample.
which was then opened to the pumps. After a short time, the adapter stopcock was closed and the bulb stopcock opened. Almost immediately crystals of methyl phenyl thiourea began to form according to the reaction:

\[ C_6H_5-N=\text{C} \equiv \text{S} + \text{C}^{15}H_3\text{NH}_2 \rightarrow C_6H_5-N\equiv\text{C}=\text{NH}^\text{iN} \text{H}_3. \]

This reaction mixture was allowed to stand overnight, following which the tube containing the derivative was removed. The excess phenyl isothiocyanate was removed and the crystals of derivative triturated five times with 2 ml. portions of hexane, which were removed with capillary pipettes. The crystals were then dissolved in 1-2 ml. of methanol which was then evaporated in a jet of nitrogen.

In order to insure the purity of the derivative crystals, fractional crystallizations were carried out using the two solvent pairs, methanol-water and benzene-hexane. It was found that one crystallization with each of these pairs was sufficient to bring about constant specific activity of the derivative. To carry out a crystallization, the derivative was dissolved in the first member of the solvent pair at 50°C in a water bath. The second member of the pair was then added drop by drop until a turbidity developed, then one more drop of the first member was added. The crystals that precipitated out on cooling were centrifuged out and the liquid removed with a capillary pipette. The crystals were then dried in vacuo over P_2O_5 at 78°C.

Combustion and counting of the methyl phenyl thiourea derivatives followed the method of Van Slyke, Steele and
DATA AND RESULTS


Figures 9, 10, 11, and 12 show the major results of chromatographic column studies. The data of figure 12 was obtained using the Perkin Elmer Vapor Fractometer. The other curves were obtained with the chromatograph built in this laboratory.

2. Analysis of Brookhaven Samples.

Due to errors in procedure only a very small amount of methyl phenyl thiourea derivative of one of the Brookhaven samples was obtained. This sample was the one which contained carrier methyl amine. Unfortunately the amount of derivative obtained was too small to be combusted and counted accurately. A derivative was correctly formed for the other sample. This sample contained no initial methyl amine carrier. Table 1 shows the data and results of analysis of this sample. The percent apparent bond retention of 18.5% was calculated by the method used by Wolfgang, Anderson, and Dodson.


The C\textsuperscript{14} ethane used for the radiation induced exchange studies was that obtained from the Brookhaven samples. This consisted of 53 ml.-cm, containing 27.4 mole percent C\textsuperscript{14} and 56.7 ml.-cm.* containing 16.5 isotopic percent C\textsuperscript{14}. These

* As the work outlined in this thesis was carried out at 25 ± 1\textdegree C, all PV values herein are considered as being at 25\textdegree C.
were mixed together to give 109.7 ml.-cm. containing 21.8 isotopic percent C$^{14}$.

Tables 2, 3, 4, and 5 give the data and results of the exchange study samples. Three series of samples were irradiated and analyzed.

Series 1 samples had variable times of irradiation with carbon-14 ethane and methyl amine contents being constant.

Series 2 had essentially a constant time of irradiation and a constant amount of carbon-14 ethane while methyl amine content was varied. There was some slight variation in some of the times of irradiation of this series, but it is small enough to be considered insignificant.

Series 3 samples had variable carbon-14 ethane content and constant methyl amine content and time of irradiation.

In tables 2, 3, and 4 the third column labelled, "final methyl amine", lists the total amount of methyl amine present after the carrier amount had been added in analysis, i.e. methyl amine recovered from the irradiated sample plus that added in analysis. The fourth column labelled, "combustion sample", lists the milligrams of carbon found in each combustion sample by the Van Slyke manometric method.

Table 5 lists the results, calculated as shown below, from the exchange data. Column 3 lists the count for the total amount of methyl amine present during the irradiation. Column 4 lists the specific activity with respect to the amount of methyl amine present during the irradiation.
Figures 13-20 are various curves obtained using the data of the exchange runs.

4. Irradiation Product Analysis.

Four samples consisting of 4.86 ml.-cm. of $\text{C}^{14}$ ethane and 96 ml.-cm. of methyl amine were irradiated for various times. Following removal from the source, these were analyzed on the Vapor Fractometer, using the ionization chamber detector. The data for samples B, C, and D is listed in table 6. The retention values are calculated from the ionization chamber curves. Sample A showed no peaks from the ionization detector, and hence is not listed. Samples B, C, and D all showed a peak at a retention volume near 515 ml. Other peaks appeared in some runs but were not consistent from sample to sample. Figures 21 and 22 show the Vapor Fractometer curve and the ionization chamber detector curve respectively for sample D. The dotted peak in figure 22 is one of those which did not appear in any of the other sample analyses.
GAS CHROMATOGRAPHIC CURVE
FOR
DOW 550-10% HENDECANOL PACKING
65°C.  15 ml./min. FLOW RATE

![Graph showing gas chromatographic curve for Dow 550-10% Hendecanol packing at 65°C with a flow rate of 15 ml./min. The graph indicates the detection of air, methyl amine, ethyl + dimethyl amines over time (minutes).]

FIGURE 9

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.
GAS CHROMATOGRAPHIC CURVE
FOR
DOW 550-10% HENDECANOL
ROOM TEMP. 15 ml./min. FLOW RATE

FIGURE 10

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.
GAS CHROMATOGRAPHIC CURVE FOR 
o-TOLUIDINE PACKING 
50°C. 60 ml./min. FLOW RATE

FIGURE 11
TABLE 1
BROOKHAVEN SAMPLE A

<table>
<thead>
<tr>
<th>Original sample composition:</th>
<th>64 ml.-cm. of C\textsuperscript{14} ethane</th>
</tr>
</thead>
<tbody>
<tr>
<td>Isotopic % carbon-14:</td>
<td>16.5</td>
</tr>
<tr>
<td>Time of self decay:</td>
<td>4.5 years</td>
</tr>
<tr>
<td>Ethane recovered:</td>
<td>56.7 ml.-cm.</td>
</tr>
<tr>
<td>Carrier methyl amine added:</td>
<td>879.7 ml.-cm.</td>
</tr>
<tr>
<td>Counting (tube #4):</td>
<td>58,478</td>
</tr>
<tr>
<td></td>
<td>59,734</td>
</tr>
<tr>
<td></td>
<td>58,974</td>
</tr>
<tr>
<td>Total sample count:</td>
<td>412 dis./sec.</td>
</tr>
</tbody>
</table>

Percent bond retention was calculated by the formula\textsuperscript{5},

\[
q = \frac{\text{sample count}}{K^2P^2NT}
\]

where, 
- \(K\) = decay constant. 
- \(P\) = fractional isotope abundance of C\textsuperscript{14} in ethane. 
- \(N\) = total number of carbon atoms in ethane. 
- \(T\) = time of self decay.

Thus,

\[
q = \frac{4.12 \times 10^2}{(3.95 \times 10^{-12})^2(.165)^2(3.66 \times 10^{18})(4.5)(365)(86,400)} = 0.185
\]

Therefore percent bond retention is 18.5%
**TABLE 3**

**Series 2**

**EFFECT OF VARYING METHYL AMINE UPON EXCHANGE**

Ethane Content: 4.86 ml.-cm.  Irradiation Time: 272-280 hours

<table>
<thead>
<tr>
<th>Sample</th>
<th>Original Methyl Amine (ml.-cm.)</th>
<th>Final Methyl Amine (ml.-cm.)</th>
<th>Combustion Sample (mg. of carbon)</th>
<th>Net Counts/hour</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>60.1</td>
<td>904</td>
<td>1.96</td>
<td>73,166</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>73,121</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>73,251</td>
</tr>
<tr>
<td>B</td>
<td>96</td>
<td>953</td>
<td>2.45</td>
<td>69,912</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>69,809</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>69,693</td>
</tr>
<tr>
<td>C</td>
<td>150</td>
<td>906</td>
<td>2.13</td>
<td>37,685</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>37,623</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>37,807</td>
</tr>
<tr>
<td>D</td>
<td>203</td>
<td>908</td>
<td>2.05</td>
<td>20,074</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>20,560</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>20,597</td>
</tr>
<tr>
<td>E</td>
<td>252</td>
<td>869</td>
<td>2.31</td>
<td>18,856</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>18,513</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>19,194</td>
</tr>
</tbody>
</table>

(Continued on next page.)
<table>
<thead>
<tr>
<th>Sample</th>
<th>Original Methyl Amine (ml.-cm.)</th>
<th>Final Methyl Amine (ml.-cm.)</th>
<th>Combustion Sample (mg. of carbon)</th>
<th>Net Counts/hour</th>
</tr>
</thead>
<tbody>
<tr>
<td>F</td>
<td>46</td>
<td>944</td>
<td>2.11</td>
<td>86,291, 86,415, 86,327</td>
</tr>
<tr>
<td>G</td>
<td>13.8</td>
<td>831</td>
<td>2.01</td>
<td>2,248, 2,518, 2,162</td>
</tr>
<tr>
<td>H</td>
<td>23.3</td>
<td>838</td>
<td>2.09</td>
<td>5,916, 5,867, 5,816</td>
</tr>
<tr>
<td>Series</td>
<td>Sample</td>
<td>Total Sample Count (dis./sec.)</td>
<td>Disintegrations/sec./mg. of CH₃NH₂</td>
<td></td>
</tr>
<tr>
<td>--------</td>
<td>--------</td>
<td>-------------------------------</td>
<td>-----------------------------------</td>
<td></td>
</tr>
<tr>
<td>1.</td>
<td>A</td>
<td>220</td>
<td>137</td>
<td></td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>338</td>
<td>211</td>
<td></td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>468</td>
<td>292</td>
<td></td>
</tr>
<tr>
<td></td>
<td>D</td>
<td>717</td>
<td>448</td>
<td></td>
</tr>
<tr>
<td></td>
<td>E</td>
<td>1285</td>
<td>802</td>
<td></td>
</tr>
</tbody>
</table>

| 2.     | A      | 575                           | 564                               |
|        | B      | 461                           | 288                               |
|        | C      | 274                           | 109                               |
|        | D      | 153                           | 45.2                              |
|        | E      | 121                           | 28.7                              |
|        | F      | 655                           | 851                               |
|        | G      | 16.35                         | 70.7                              |
|        | H      | 40                            | 103                               |

(Continued on next page.)
SERIES 1: TOTAL ACTIVITY AS A FUNCTION OF IRRADIATION TIME

FIGURE 13
SERIES 2: SPECIFIC ACTIVITY AS A FUNCTION OF METHYL AMINE CONCENTRATION

DISINTEGRATIONS/SEC./MG. CH3NH2

ML.-OM. METHYL AMINE

FIGURE 16
SERIES 3:
SPECIFIC ACTIVITY AS A FUNCTION OF ETHANE CONCENTRATION

FIGURE 18
SERIES 3:
TOTAL COUNT AS A FUNCTION OF (ML. - Cm. ETHANE)^2

FIGURE 19

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.
SAMPLE 4-D VAPOR FRACOMETER CURVE

o-TOLUIDINE COLUMNS, ROOM TEMP., 27 ML./MIN. FLOW RATE

Methyl amine

Ethane

TIME (Minutes)

6 12 18

RELATIVE POTENNIOMETER DEFLECTION
SAMPLE 4-D IONIZATION CHAMBER CURVE

CHAMBER RESISTANCE 0.98 x 10^13 Ohms

POLARIZING POTENTIAL 9 VOLS

Ethane

Methyl amine

Unidentified

TIME (Minutes)

log of relative potentiometer deflection

FIGURE 22

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.
CONCLUSIONS

1. Column Packing Studies.

The intent of column packing studies was to arrive at a packing that will separate methyl, dimethyl, and ethyl amines from one another. Such a column should also afford separation of ethane from the amines. All columns studied in this work produced an excellent separation of ethane from the amines. Efficient amine separations, on the other hand, proved somewhat more of a problem. Shonting\textsuperscript{11} found that the separation of methyl amine from dimethyl and ethyl amines could easily be done, but he found no efficient packing to separate ethyl and dimethyl amines. As figures 9 and 10 indicate, a Dow 550 silicone fluid-10\% hendecanol packing did not solve this problem at either room temperature or 65°C. Indication of a better separation was shown by a packing of o-toluidine at 50°C. (figure 11). Further work showed that an o-toluidine packing at room temperature can be used to produce a usable separation of the three amines (figure 12).

2. Analysis of Brookhaven Samples.

The two gas phase samples which had been prepared at Brookhaven Laboratories afforded an opportunity for a study of the effect of long grow-in periods on apparent methyl amine bond retention. Unfortunately, no significant results could be obtained for the sample that had carrier methyl.
amine present during the grow-in period. The other sample, which originally consisted of C\textsuperscript{14} ethane alone, could be analyzed. The results of this analysis are quite significant. As can be seen in figure 1, there is a decrease in bond retention with increased grow-in time. The low apparent bond retention (18.5%) of this relatively long grow-in time sample upholds these previous data.

A possible explanation of the dependence of bond retention on grow-in time would be a self irradiation effect on the methyl amine. A methyl amine molecule which survives after decay of a carbon atom of doubly labelled C\textsuperscript{14} ethane may later be caused to decompose by the energetic beta particle emitted from another decaying C\textsuperscript{14} atom in the system. As methyl amine concentration increases with increased grow-in time, the probability of a beta particle in the system acting upon a methyl amine molecule increases. If the interaction between beta particle and methyl amine results in decomposition of the molecule, an effect of grow-in time on apparent bond retention is to be expected. There appears to be no other reasonable explanation of this effect. Wolfgang et.al.\textsuperscript{3} however, in one of their samples increased self irradiation by a factor of about twenty and found no significant effect on the apparent bond retention results. This is an area ripe for further work. In the first place, more work should be done to either prove or disprove the trend of decreased apparent bond retention with grow-in time. A study of radiation
Figures 17 and 18 show linear relationships at higher pressures of ethane between total count and amount of ethane and specific activity and amount of ethane. At lower amounts of ethane these relationships are not linear. Figure 19 shows a definite linear relationship between total count and the square of the ml.-cm. of ethane at the lower ethane concentrations. Figure 20 indicates a linear relationship between atoms of carbon-14 exchanged per 100 electron volts absorbed by ethane ("G" value) and the amount of ethane.

The results discussed above are explainable by the following mechanism:

\[
\begin{align*}
  & E \xrightarrow{\gamma} E^* \\
  & E^* + M \rightarrow M^* + E \\
  & E^* + E \rightarrow E + E^* \\
  & E^* \rightarrow C^{14}H_3^* + \ldots \ldots \ldots \\
  & M \xrightarrow{\gamma} M^* \\
  & M^* \rightarrow CH_3^* + NH_2^* \\
  & C^{14}H_3^* + NH_2^* \rightarrow C^{14}H_3NH_2
\end{align*}
\]

E represents ethane
M represents methyl amine
* denotes an excited or ionized state

The results of the exchange studies support such a mechanism as that above. In the first place it would certainly be expected that increased irradiation would increase the amount of exchange as was found in the results of series 1
various investigators\textsuperscript{12} to be in the range of 8.97-9.41 electron volts, whereas that of ethane has been found\textsuperscript{13} to be in the range of 12.71-13.05 electron volts.

The results of series 3 (figures 17, 18, and 19) would also support the mechanism. Figures 17 and 18 indicate that the exchange is first order in ethane at higher concentrations and other than first order at lower concentrations. Figure 19 indicates that the exchange is second order in ethane at lower concentrations and other than second order at higher concentrations. These results can be explained by two considerations of the mechanism above. At higher ethane concentrations the exchange determining factor is step (1), the activation of ethane. This results in a first order dependence on ethane. At lower ethane concentrations consideration must be made not only of step (1), but also the competition of step (3) with step (2). Step (2) decreases the exchange by deactivation of the ethane before it can react as in step (4). Step (3) does not decrease the final exchange. Thus, at the lower ethane concentrations, the exchange depends not only upon the ethane activation step (1), but also upon the extent to which steps (3) and (4) can predominate over step (2). This is analogous to the pressure dependence found in unimolecular rate processes\textsuperscript{14}, the reaction being first order at high pressures and second order at low pressures. As the pressure of ethane increases, (3) increases more rapidly than (2) with a resulting increase in the exchange. Figure 20 shows an increase of "G" value.
of the exchange with increased ethane content. As ethane content increases, energy absorbed by ethane is retained in an ethane molecule due to (3), rather than lost as in (2). In other words, the relative frequency of (3) increases with respect to (2). The result of this would be an increase in "G" value as observed.

The above mechanism is not the only one possible. Consideration should especially be given to ion-molecule reactions which have lately been considered of increasing importance in radiation chemistry of the gas phase. Some of the steps in a mechanism might well be of this ion-molecule type. Examples of some possibilities are:

$$M^+ + M \rightarrow \text{products other than } C^{14}H_3NH_2.$$  
$$M^+ + E \rightarrow C^{14}H_3NH_2 + \ldots \ldots \ldots\ldots\ldots\ldots\ldots$$  
$$E^+ + M \rightarrow C^{14}H_3NH_2 + \ldots \ldots \ldots\ldots\ldots\ldots\ldots$$  
$$E^+ + E \rightarrow \text{products other than } C^{14}H_3NH_2.$$

Various mechanisms containing some of these steps could also be explained by the data obtained in this work. Further studies of such reactions might aid in determination of the mechanism of carbon-14 exchange between ethane and methyl amine.

The question now arises as to the effect of the exchange on the bond retention studies of Wolfgang, Anderson, and Dodson. From the results obtained in this thesis work it is impossible to say anything quantitative about this, and qualitatively it is possible to say only that exchange might have affected the bond retention results. The un-
amounts of the non-carbon-14 containing products to be detectible would require an absurdly long period of irradiation. However, since determination of radioactivity is relatively sensitive, it was thought that detection of carbon-14 containing products was within the realm of possibility. The use of a radiation detector in conjunction with the Vapor Fractometer enabled this to be attempted, and the results are shown in table 6. Figures 21 and 22 show the Vapor Fractometer curve and the ionization detector curve for a sample thus analyzed. This sample (4-D) was the only one to show a methyl amine peak by the Fractometer detector. The reason samples 4-B and 4-C did not show such a peak is probably that the Fractometer recorder was quite far out of balance at the start of the runs. The data shows that samples B, C, and D all showed peaks on the ionization chamber detector. It should be noted that only one peak occurred consistently for all three samples. The other peaks that occurred could not be duplicated from sample to sample. The essentially constant retention volume of the common peak and its value indicate that this is methyl amine. All three samples also very nicely show the ethane activity. The other peaks, since they were not reproducible, must be considered as being due to factors other than carbon-14 containing products, i.e., vibrations, alpha background radiation.

It thus appears that with the radiation doses here employed, the only materials detectible by the ionization
SUMMARY

The following main points have been developed as a result of the work described in this thesis:

1. The extent of radiation induced carbon-14 exchange from ethane to methyl amine is directly proportional to absorbed radiation.

2. More than one factor affects the amount of radiation induced exchange of carbon between ethane and methyl amine as methyl amine concentration is varied. At relatively lower concentrations one factor is dominant, whereas at relatively higher methyl amine concentrations another factor is dominant. As these factors influence the amount of exchange in opposite directions, there must be an optimum methyl amine concentration for the exchange.

3. The amount of radiation induced carbon-14 exchange from ethane to methyl amine is second order in ethane at lower ethane concentrations and first order in ethane at higher ethane concentrations.

4. Product analysis of irradiated samples of carbon-14 ethane and methyl amine, using a gas chromatograph in conjunction with an ionization chamber detector, shows only the original ethane and product carbon-14 methyl amine.

It must be kept in mind that the four above results strictly apply only to the radiation doses and concentrations used in the experimental work.

A mechanism, consistent with the above points, has been suggested.
BIBLIOGRAPHY


**BIOGRAPHICAL DATA**

<table>
<thead>
<tr>
<th>Name in Full:</th>
<th>Philip Shepard Lamprey</th>
</tr>
</thead>
<tbody>
<tr>
<td>Date of Birth:</td>
<td>August 23, 1934</td>
</tr>
<tr>
<td>Place of Birth:</td>
<td>Salem, Massachusetts</td>
</tr>
<tr>
<td>Secondary Education:</td>
<td>Chelmsford High School, Chelmsford, Massachusetts</td>
</tr>
<tr>
<td>Collegiate Institutions Attended:</td>
<td>Dates</td>
</tr>
<tr>
<td>Lowell Technological Institute</td>
<td>1952-1956</td>
</tr>
</tbody>
</table>