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The effect of beta decay of a constituent carbon atom of the ethane molecule has been studied by a technique of double labeling, with $C^{14}H_3C^{14}H_3$. The radioactivity of one of the carbon atoms served as a tracer for the entity which results from the decay of the other to nitrogen when the chemical bond is preserved. It was found that in 47% of the cases the molecular entity was not disrupted but survived as methyl amine, $C^{14}H_3NH_2$. This result is in good agreement with theoretical expectations.

INTRODUCTION

THE rupture of chemical bonds when an atom in a molecule undergoes a nuclear transformation is a well-known phenomenon. Typically, the transformation gives a product atom of high kinetic energy; this atom breaks away from its bonded partners and moves through the system losing energy by collisions. At some stage it may become stably attached to new partners. This collection of effects is the subject of the field of study known as "hot atom chemistry."[1]

In contrast to the many studies which have been made of these phenomena following neutron capture ("Szilard-Chalmers reactions"), relatively few[1,2] have been made of the chemical effects of beta decay. The reason may be found in the facts that the fate of the product atom is most readily determined when it is radioactive, and that the number of convenient and interesting cases in which this prevails is relatively small.

The case of carbon-14 is of particular interest. This isotope is widely used in tracer investigations in chemical and biological systems, and also occurs at an appreciable level in the biosphere.[3] Further, since the maximum energy of the beta particles is relatively low, 0.154 Mev, the maximum recoil energy of the nitrogen-14 daughter is low, 7.0 ev; and, considering the distribution of this energy between internal motions and translation of the molecule as a whole, it would appear that the kinetic energy of recoil might be insufficient to cause bond rupture in many compounds. On the other hand, the disturbance in the arrangement of the orbital electrons caused by the change in atomic number might lead to bond rupture. In any case, there is clearly the possibility, insofar as kinetic energy of recoil is concerned, that the product nitrogen-14 atom will remain attached to its original bond partner, or partners.[4] The purpose of this study was to determine whether this occurs to an appreciable extent.[5]

Since observation of a radioactive daughter atom cannot be used in the present instance—nitrogen-14 being stable—we have devised a technique of double isotopic labeling for the purposes of the investigation. Two radioactive atoms are incorporated in the same molecule. The chemical fate of the entity remaining after the decay of one of them is traced by the radioactivity of the other.[6] The system chosen was doubly labeled ethane, $C^{14}H_3C^{14}H_3$, which molecule, if not disrupted, decays to radioactive methyl amine, $C^{14}H_3NH_2$. A gaseous system was chosen in order to minimize chemical reactions subsequent to the transition of interest and tending to obscure it. Ethane and methyl amine, in particular, are suitable since they are stable and easily separated by gentle techniques, thus making exchange of activity unlikely. Furthermore this system is sufficiently simple to make it relatively amenable to theoretical treatment.

The procedure used can be summarized very simply. $C^{14}H_3C^{14}H_3$ was prepared. The gaseous compound was allowed to stand for a suitable time, after which CH_3NH_2 carrier was added, separated, and exhaustively purified. From the amount of C^{14} activity in the purified methyl amine, or its derivatives, the fraction of the radioethane molecules that, on undergoing $C^{14} \rightarrow N^{14}$ decay, fail to dissociate and hence become methyl amine molecules, can be calculated.

This technique is evidently capable of a number of variations. It need not be restricted to cases in which the two radioactive atoms are C^{14}, nor need the two

* Research performed under the auspices of the U. S. Atomic Energy Commission.

[1] For a recent review of the field see J. E. Willard, Ann. Revs. Nuclear Sci. 3, 193–220 (1953).

[2] a. T. H. Davies, J. Phys. Chem. 52, 595 (1948). b. Burgus, Davies, Edwards, Gest, Stanley, Williams, and Coryell, J. chim. phys. 45, 165 (1948). c. W. H. Burgus and J. W. Kennedy, J. Chem. Phys. 18, 97 (1950). d. F. J. Keneshea and M. Kahn, J. Am. Chem. Soc. 74, 5254 (1952). e. Edwards, Day, and Overman, J. Chem. Phys. 21, 1555 (1953).

[3] Libby, Anderson, and Arnold, Science 109, 227 (1949).

[4] The theory of electronic, vibrational, and rotational excitations of a diatomic molecule due to beta decay in a constituent atom has been worked out in some detail by M. Wolfsberg, J. Chem. Phys., 24, 24 (1956). Wolfsberg concludes that there is a significant probability of nonrupture in the C^{14} case.

[5] Our interest was first directed to this problem in speculative conversation with Professor H. C. Urey, in the summer of 1947, on the possibility that the conversion of carbon-carbon to carbon-nitrogen linkages in nature might have biological consequences.

[6] The method was earlier investigated at this Laboratory by W. W. Miller and R. W. Dodson with doubly labeled acetylene. This system proved unsuitable because other processes, possibly radiation chemical exchange, also led to the product of interest, $HC^{14}N$.

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atoms be isotopes of the same element. The use of tritium as one of the labels is an obvious possibility.

CONSIDERATIONS ON DOUBLE LABELING

Consider a collection of atoms of a given element' N in number, containing stable species and also a radioactive species. Suppose that the atoms are combined two at a time at random into some molecule of interest. Neglect isotopic fractionation effects. Let p be the probability that an atom in the collection is radioactive; i.e., p is the fractional isotopic abundance of the radioactive species and pN is the number of atoms of this species. Then, the numbers of molecules which contain two, one, and no radioactive atoms are, respectively, $p^2N/2$, $p(1-p)N$, and $(1-p)^2N/2$.

Suppose that the mixture of labeled molecules stands for a time t, short compared to the half-life. The number of decays in the doubly labeled species is $\lambda p^2 Nt$, where λ is the radioactive decay constant. If in each decay the probability that molecular integrity is retained is q, the number of molecules whose integrity has been retained during these decay processes is $q\lambda p^2 Nt$. The radioactive disintegration rate of these molecules is $q\lambda^2 p^2 Nt$, or qA^2t/N, where A is the total disintegration rate, λpN. Note that the last expression does not directly involve the decay constant or abundance of the tracer isotope. It is not necessary in this application of double labeling that the abundance of the tracer be so high that a substantial fraction is in the doubly labeled molecules, i.e., materials of quite short half-life may be used. All that is required in the way of isotopic composition and properties is that the half-life, activity, and specific activity are large enough that A^2t/N is a measurable disintegration rate.

It is worth mentioning that a similar result follows when radioactive isotopes of two different elements are used for double labeling. Consider a molecule XYR, where X and Y denote the two radioactive elements. The radioactivity due to tracer X in the molecule formed by the decay of radioactive Y to a new species is $A_X A_Y t/N_X$, where A_X and A_Y are the total activities due to X and Y and $N_X(=N_Y)$ is the total number of atoms of X.

EXPERIMENTAL

The basic experimental difficulty is that at the end of the experiment the ratio of product to reactant is of the order of 10^{-5}, in terms of both mole fraction and radioactivity. Hence great care has to be taken to ensure the identity and the origin of the product. The experimental procedure has accordingly been devised throughout with the objective of avoiding ambiguities of such a nature. The main features of the procedure to be described are: counting the C^{14}; preparation and purification of the active ethane; growing in and separation of product; purification and identification of the product.

Counting the C^{14}

Active samples were counted in the form of CO_2 in a methane- or methane-argon-filled proportional counter in all but some preliminary experiments in which solid samples were counted in a Nucleometer. The counting arrangement[7] and the procedure[8] for preparing the CO_2 samples have been described in detail elsewhere. The counter tubes were glass cylinders, 35 cm long and 2.4 cm in diameter, with cathodes of deposited silver approximately 30 cm long. The cathode volume of each tube was determined by filling with toluene. The basic calibration for the determination of absolute counting rates was established by measurements of aliquots of an active sodium carbonate solution distributed by the National Bureau of Standards ("Carbon-14 Beta Ray Standard. Sodium carbonate solution—1280 dps/ml, NBS Series A, June, 1944.").

The backgrounds were about 70 counts per minute and are considered to be known to a standard deviation of 2 counts per minute. Sample counting rates ranged from 20 to 2000 counts per minute for carbon samples weighing 0.5 to 5 mg.

Preparation of the Radioethane

The ethane used in series A was prepared from a $CaCO_3$ sample obtained from Oak Ridge, nominally containing 15.2 isotopic percent C^{14}. That used in series B and C was prepared from a $BaCO_3$ sample obtained from Oak Ridge, nominally containing 25.2 isotopic percent C^{14}. From our measurements the ethane assayed 16.6 isotopic percent C^{14} for A, 26.6 isotopic percent for B, and 27.4 isotopic percent for C.

Preparations were carried out in batches of 40–100 micromoles containing 1 to 2 millicuries according to the sequence

$$BaCO_3 \xrightarrow{H_2SO_4} CO_2 \xrightarrow{Ba} Ba_2C \xrightarrow{H_2O} C_2H_2 \xrightarrow[Pd]{H_2} C_2H_6.$$
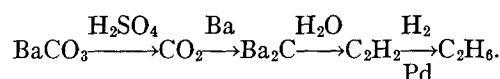
The vacuum line is shown in Fig. 1. CO_2 was evolved from a weighed portion of $BaCO_3$ by reaction with concentrated H_2SO_4 in the Y tube. The CO_2 was then reacted with an excess of very pure barium,[9] to give barium carbide, in the stainless steel furnace, C. This apparatus and procedure were essentially as described by Arrol and Glascock.[10]

The Ba_2C was hydrolyzed by distilled water introduced dropwise from bulb D. The evolved gases were slowly passed through trap E at $-78°C$ and then into trap F at $-196°C$. The acetylene was distilled by warming trap F at $-160°C$ and condensed into the gas buret, which was chilled to $-196°C$. The acetylene was

[7] W. Bernstein and R. Ballentine, Rev. Sci. Instr. 21, 158 (1950).
[8] Anderson, Delabarre, and Bothner-By, Anal. Chem. 24, 1298 (1952).
[9] Obtained from Varlacoid Chemical Company and stated to be 99.9+% pure.
[10] W. J. Arrol and R. Glascock, J. Chem. Soc. 1534 (1948).

FIG. 1. Radioethane preparation and purification line.

then reduced to C_2H_6 with two volumes of H_2 over palladized palladium in vessel G. The catalyst and reduction procedure followed suggestions of Glascock.[11] The product was examined mass spectrometrically and contained of the order of 5–10% butane. It was stored over concentrated H_2SO_4 for several days, then distilled from a bath at $-160°C$. Vapor pressure, mass spectrometer, and infrared measurements showed that the ethane was better than 99% pure.

The amount of ethane was determined by pressure-volume measurements. For C^{14} assay an aliquot was taken and diluted by a factor of about 10^8 as follows. The ethane was allowed to fill the calibrated bulbs H and I at the same temperature and pressure. The stopcock between the bulbs was closed, and the ethane in H was removed. Bulb H was then filled with inactive ethane at a known temperature and pressure. Mixing was accomplished by several cycles of condensing the contents of both bulbs together and re-evaporating. An aliquot of the diluted mixture was transferred to a Vycor combustion tube containing CuO, and oxidized to CO_2 at 700–$750°C$. The CO_2 was again diluted in a separate vacuum line and was then counted as described earlier. The moles of CO_2 found at this point agreed with the amount expected from the amount of ethane taken to within about 2%.

Growing-in and Separation of Product

One liter Pyrex glass bulbs were generally used for storing the active ethane. The relatively large size was employed in order to minimize self-irradiation of the sample. The gas was at a pressure of about 1 mm. Under these conditions each beta ray produces, on the

average, only about three ion pairs before reaching the wall.

In all but one of the experiments the radioethane was stored without methyl amine, and this carrier was only added at the end of the experiment, when the $C^{14}H_3NH_2$ was to be separated. In run A–f, however, it was shown that the presence of CH_3NH_2 during storage does not affect the results obtained (there was no exchange with radioethane).

The vacuum line shown in Fig. 2 was used. Stopcock grease was kept at a minimum by the use, wherever possible, of mercury cut-off valves.

Before storing a new sample of ethane any $C^{14}H_3NH_2$ which had already grown in was removed. In order to accomplish this, the ethane and a known quantity of methyl amine were put into vessel R on the line and mixed by gentle warming of the side of the vessel. The mixture was then frozen down with liquid nitrogen in trap L. A bath of melting isopentane was placed around trap L and the ethane drawn into gas buret P by means of liquid nitrogen in trap Q. As always following a separation, the quantities of methyl amine and ethane separated were then measured to be sure that the distillation had been a clean one. To remove any remaining trace of methyl amine the ethane was then stored for several hours in vessel R, which now contained concentrated, degassed H_2SO_4. Finally the sample was distilled into the liter bulb N fitted with several break-off seals and constrictions as shown. The bulb was sealed off, removed from the line and stored in the dark.

After standing for some weeks or months the system was "milked" for $C^{14}H_3NH_2$ by the following procedure. The bulb was attached to the line through one of its arms containing a break-off seal and a constriction. If the sample did not already have carrier methyl amine mixed with it, methyl amine was allowed to enter the bulb when the break-off seal was opened. In this case the gas was mixed by gentle warming of the side of the vessel. The mixture was condensed into trap L. The

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[11] R. Glascock, private communication. The palladium catalyst was palladized by acting as cathode in the electrolysis of saturated palladium chloride solution containing 0.02% lead acetate. The deposited palladium was then activated by further electrolysis using very dilute H_2SO_4 as electrolyte. The hydrogenation was carried out at room temperature and about atmospheric pressure.

ethane was distilled away from the methyl amine by warming the trap to $-160°C$ with a bath of melting isopentane, the ethane being stored in buret P. The methyl amine fraction was then "washed" by mixing with inactive ethane, and this ethane was discarded after separation. This was repeated once. Finally the methyl amine was condensed in a small bulb attached to the line at S. A further measured amount of inactive CH_3NH_2 was added to bring the total quantity of material to about 15 mg, and the sample was then removed from the line for further purification and assay.

Two experiments were done to determine the completeness with which the $C^{14}H_3NH_2$ was removed from the ethane by the carrier CH_3NH_2. These consisted of doing a second milking about five hours after the first following runs $A–f$ and $B–c$. The activities found from the assay of the purified amine derivative were $12\pm6\%$ and $16\pm2\%$ of those found in $A–f$ and $B–c$, respectively. The amounts of carrier recovered, as determined by pressure-volume measurement, were $100\pm2\%$ and $90\pm2\%$ in $A–f$ and $B–c$, respectively. These effects may be due in part to adsorption of methyl amine on the walls. The percent recovery of the carrier was determined in every milking, and the final result of each milking was corrected in case of incomplete recovery. From the results just mentioned, it is not certain whether this correction is sufficient to account for all of the active methyl amine. This uncertainty is reflected in the estimate of error which we attach to our final result.

Final Purification of the Product

The procedure for identifying and measuring methyl amine-C^{14} obtained by the milking procedure was to synthesize a solid derivative of the amine and rigorously to purify this derivative by repeated sequential crystal-lizations until constancy in specific activity was obtained. The crystallizations were fractional crystallizations in the sense that a substantial portion of the material remained in solution in each case. However, in a given fractionation, only one crystal crop was taken.

The following conditions were placed on the choice of a suitable derivative: the reactions producing it must be clean-cut and quantitative; the derivative must be a solid amenable to recrystallization on a micro or semimicro scale; and it must be reasonably different in its physical properties, such as melting point, vis-a-vis possible radioactive amine-like contaminants. Methyl phenyl thiourea, which is produced by the direct reaction of gaseous methyl amine and liquid phenyl isothiocyanate according to the reaction

$$C_6H_5-N=C=S + C^{14}H_3-NH_2 \rightarrow$$

$$\begin{matrix} & & S \\ & H & \| & H \\ C_6H_5-N-C-N-C^{14}H_3, \end{matrix}$$
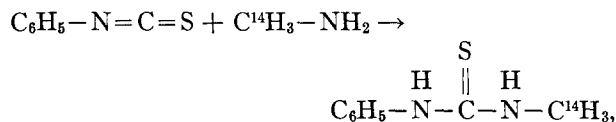
was chosen as the derivative. In contrast to the aryl isocyanide, the thio analogue is relatively insensitive to water, and the possible reaction to give di-aryl thiourea is not troublesome. Also the possible contaminant amines have derivatives with sufficiently different melting points so that it is reasonable to expect that crystallization would markedly separate them. The thiourea from methyl amine melts at $115°C$, that from dimethyl amine at $135°C$ and that from ethyl amine melts at $106°C$. The trimethyl amine, of course, will not form a derivative of this type at all.

The initial amount of derivative was about 80 mg; solvent pairs were used to reduce losses of material. The solvent pairs mainly used were methanol-water and benzene-hexane. The first pair tends to retain polar impurities in solution; the second tends to retain non-
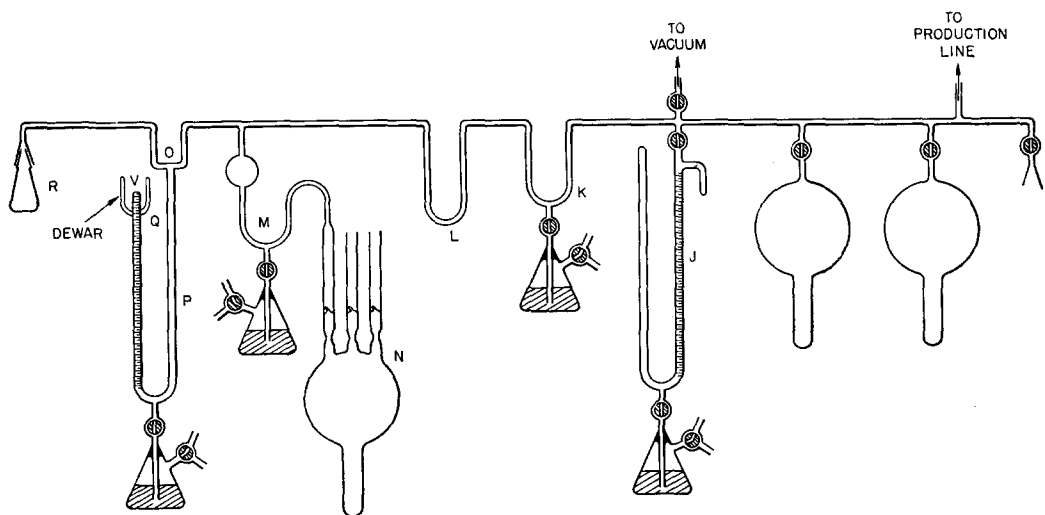
NOTE: K, M+O ARE Hg CUT-OFF VALVES

FIG. 2. Vacuum line for milking methyl amine from radioethane.

polar organic contaminants. The crystallizations were done in alternation between the solvent pairs, a radio-assay being performed on each crystal crop.

To prepare the methyl phenyl thiourea, a milking bulb containing approximately 15 mg of methyl amine was attached to a small tube having a side arm with stopcock, the tube having been charged with 0.30 ml of reagent grade phenyl isothiocyanate. The assembly, excluding the amine bulb, was evacuated to 1 mm and the stopcock to the pump shut off. The amine was then allowed to diffuse to the reagent. An immediate reaction occurs, heat is liberated, and within a minute or two crystals of the thiourea appear. The reaction mixture was allowed to stand overnight; then air was admitted and the reaction tube removed. The mixture was thoroughly triturated five times with 2-ml portions of hexane. (All the solvents in this work were freshly re-distilled to remove nonvolatile impurities.) Each hexane wash was removed by capillary pipettes. The white crystals remaining were dissolved in 1 ml of methanol and transferred with several washings to a tared centrifuge cone. The solvent was removed by evaporation under a jet of filtered nitrogen. The crystalline residue was weighed. The yield of derivative ran between 90 and 98%. The melting point was usually above 113°C (hot stage) at this point. Upon one recrystallization and after subsequent recrystallizations the melting point invariably held at 115–115.5°C in agreement with an authentic sample of methyl phenyl thiourea prepared and purified on a large scale.

To recrystallize the derivative, a few tenths of a milliliter of the chosen solvent, (say, methanol) was added to the material in the centrifuge cone, and the mixture was gently warmed in a water bath at 50°C to effect solution. The second solvent of the pair (in this case, water) was then added dropwise at 50°C until a slight turbidity resulted. Then a fraction of a drop of methanol was added to clear the solution completely. The crystals which soon appeared on cooling were centrifuged out, and the supernatant liquid was with-drawn. The crystals were dried at 78°C in vacuo over P_2O_5 for 30 minutes. From such a crop approximately 4–6 mg were removed for combustion and radio-assay, while the remainder was then recrystallized. The yields from each crystallization were purposely varied from 30 to 90% by control of the solvent ratio. From two to six recrystallizations were done. Precautions were taken to exclude contamination of the materials by the ordinary dust and fabric linters in the atmosphere; and the crystallizations were occasionally preceded by filtration of the solutions through sintered glass funnels. If the first hexane washes were thorough, the radio-assays leveled off at the first or second recrystallization. The variations after that were within the limit of the combined errors of analysis and assay.

For analysis and assay the methyl phenyl thiourea crystals were subjected to dry combustion to carbon dioxide, water, and oxides of nitrogen and sulfur, as elsewhere[8] described.

A test was made of the efficacy of the crystallization techniques employed for purifying the methyl phenyl thiourea. For this purpose a mixture of radioactive ethyl phenyl thiourea and diethyl phenyl thiourea was synthesized from ethanol-2-C^{14} (Tracerlab), through the steps: ethanol→ethyl iodide $\xrightarrow[\text{conc. NH}_4\text{OH}]{\text{HI}}$ ethyl, diethyl, and triethyl amines. The amine mixture was distilled in vacuo onto potassium hydroxide pellets, and thence into an excess of phenyl isothiocyanate. Several re-crystallizations from benzene gave a crude product melting at 102–104°C (pure ethyl phenyl thiourea, mp 106°C). This was used without further purification inasmuch as any diethyl phenyl thiourea or other active contaminants would provide an additional test on the method.

Two experiments were run in parallel. The crude ethyl derivative was diluted with authentic inactive ethyl derivative in one case, and with authentic inactive methyl derivative in the second case. The quantities were (1) 0.640 mg of the active materials and 52.377 mg of authentic ethyl derivative, and (2) 1.530 mg of the active mixture and 53.680 mg of the authentic methyl compound.

In both cases the mixtures were homogenized by total solution in methanol. A radio-assay was made on mixture (2) before recrystallization. The two mixtures were recrystallized using alternate solvent pairs in a fashion which simulated in detail the technique used in working up the derivatives from the milking experiments, except, of course, that the crystal crop consisted of the ethyl compound in the sequence in which it was the bulk constituent. The results are discussed below.

RESULTS AND DISCUSSION

In all runs the methyl amine derivative obtained was radioactive. The first point to be considered is whether this activity was in fact due to $C^{14}H_3NH_2$. To recapitulate, the operations on which identification is based were: (1) the initial physical separation with CH_3NH_2 carrier, (2) carrying through the chemical step in which the amine derivative was prepared, (3) carrying and the attainment of constant specific activity in the sequence of crystallizations from alternating mixed-solvent pairs.

The attainment of constant specific activity in fractional crystallizations is commonly regarded as proof that the active material is chemically identical with the carrier. We felt, however, that the principle should be checked in the present work, at least in regard to the most likely amine contaminant, ethyl amine. The results of the confirmatory experiments are plotted in Fig. 3. The data indicate that about 15% of the activity in the crude ethyl phenyl thiourea mixture was actually in the form of ethyl phenyl thiourea. Presumably the rest was mainly diethyl phenyl thiourea. It is seen that sequential crystallizations of the ethyl compound

TABLE I. Specific activity of sequential crystallizations (disintegrations/sec mgC).

Milking	Crystallization							Value taken
	1	2	3	4	5	6	7	
A–c		1.22	0.96[a]	1.21[a]				1.13
A–d	0.75		0.62	0.57	0.61	0.72	0.56	0.61
A–e	2.35	2.04	2.27	2.00				2.10
A–f	1.27	1.04	0.89	0.88	0.98	0.97		0.96
A–h	0.69	0.52	0.42					0.47
B–a		0.52	0.96	1.26	1.11	1.11		1.11
B–c	3.92	4.47	4.26	4.22	3.77	3.85		4.07
B–e	4.14	4.37	4.33					4.33
C–a	12.1	11.9	11.4	11.1		11.3		11.4
C–b[b]	12.7	12.2						12.2

[a] Successive recrystallizations from mother liquor of recrystallization 2.
[b] Para-toluene-sulfonamide derivative prepared and recrystallized instead of methyl phenyl thiourea.

showed a sensibly constant specific activity from the first crop on. The point of main consequence, however, is the fact that the crystals of the methyl compound steadily decreased in activity. The specific activity is decreased by 36% in each crystallization, on the average; and there is no tendency for this factor to decrease.

The constant specific activity obtained in the product of the runs with radioethane had the properties of an amine, and its derivative had the properties of authentic methyl amine derivative. The latter properties, as shown by the results in Fig. 3, are sharply distinguishable from those of the ethyl amine derivative and the other active species present in our confirmatory experiments. We conclude that the presence of active methyl amine in the radioethane mixtures is established beyond any reasonable doubt, and that its amount is given by our assay procedures.

Table I gives data on the specific activities of the methyl phenyl thiourea from the runs with radioethane. These results were obtained over a two year period, and the assays were interspersed with many assays of other materials not connected with this problem.

The final results for the three different preparations of radioethane are given in Table II. The amounts of
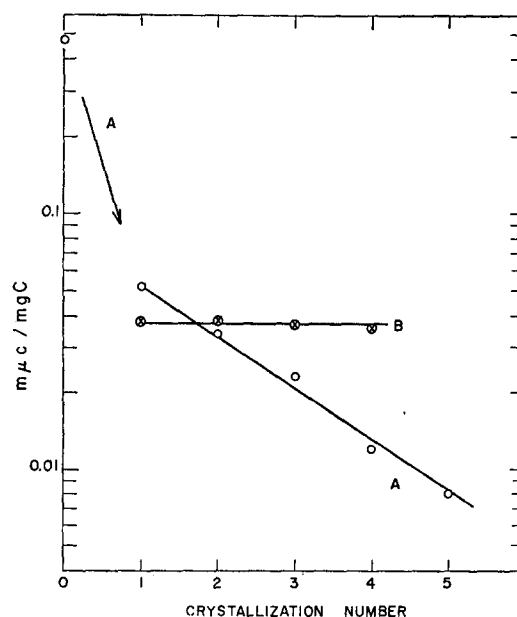
FIG. 3. Fractionation of C¹⁴-ethyl phenyl thiourea. A : methyl phenyl thiourea carrier, B: ethyl phenyl thiourea carrier.

active methyl amine found in ten different milkings, made under various conditions, are all of the order of fifty percent of the amount which would be found if every C¹⁴ decay produces a stable CH_3NH_2 molecule. The mean value is 47 ± 2. The indicated error is root mean square deviation of the set of ten individual measurements. In view of the previously mentioned uncertainty in the efficiency with which the carrier methyl amine removed the active methyl amine, we believe that the final result should be recorded as $47+7$, -2%.

In regard to errors the following may be added. There are many possible individual sources of error: both systematic and random. Some of these lie in, the pressure-volume measurements; degree of com-

TABLE II. Yield of methyl amine from doubly labeled ethane.

Milking	% C¹⁴	Amount hot ethane micromoles	Pressure mm Hg	Grow-in time days	Recovery of carrier methyl amine	Yield dis/sec	% of yield for complete retention	Mean of % of yield for complete retention, std. deviation
A–c	16.5	36.1	0.6	84	75.1%	67	50	
A–d	16.5	35.2	0.6	40	93.4%	32	51	
A–e	16.5	34.7	0.6	186	100%	100	35	47 ± 3
A–f[a]	16.5	34.4	0.6	59	100%	44	49	
A–h	16.5	33.8	65.4	31	100%	23	50	
B–a	26.6	39.1	0.7	22	98%	50	52	
B–c	26.6	38.0	0.6	134	90%	213	36.5	44 ± 4
B–e[b]	26.6[c]	37.8	3.4	104	100%	201	44.4	
C–a	27.4	80.1	1.4	109	100%	533	50.6	52 ± 1
C–b	27.4	79.9	1.4	98	100%	507	53.5	
							over-all mean	47 ± 2

[a] Methyl amine carrier present during growing-in period.
[b] 159 micromoles inactive ethane added, total micromoles =197.
[c] Exclusive of unlabeled ethane added.

pleteness of mixing the gaseous samples, of chemical conversions, and of transfers; isotopic dilution by accidental admixture of ordinary carbon during the assay procedure; contamination with C^{14}; isotopic fractionation effects; counting errors due to the inherent statistical fluctuation of decay rates; the collection of sources of systematic error in absolute beta counting. The relative standard deviation in the group of measurements for each preparation has a reasonable magnitude.

Considering the quantity qA^2t/N, it will be seen that two of the most important locations of error are in the determination of the total number of carbon atoms, N, and the determination of the absolute disintegration rate, A, of the total ethane sample. Our best guess based on experience would lead us to ascribe relative standard deviations of about 5% to the value of A and 2% to the value of N determined for each of the three preparations. The quantity A^2t/N would then be assigned a standard deviation of about 11%. The degree of concordance of the means for the three preparations is compatible with this estimate.

We may next consider the question of whether the $C^{14}H_3NH_2$ observed really arises from the direct process $C^{14}H_3C^{14}H_3 \rightarrow C^{14}H_3NH_2$. The amount of $C^{14}H_3NH_2$ is extremely small; and other very improbable processes could conceivably produce a comparable quantity of the active amine. There are several points to make about possible "spurious" processes: (1) Exchange between CH_3NH_2 and $C^{14}H_3C^{14}H_3$. This can be eliminated on the basis that the absence or presence of carrier methyl amine during the growing-in period had no appreciable effect on the results. (2) Formation of $C^{14}H_3NH_2$ by some process involving the action of radiation on the constituents of the system. This can be eliminated by the result of experiment $A-h$ (Table II). In this experiment the pressure was increased by a factor of a hundred, and hence the self-irradiation was increased by a factor of about twenty. No significant alteration in the results was found in this experiment, or in others having a smaller, but appreciable, variation in the radiation dosage. We therefore conclude that radiation chemical effects were inconsequential. (3) Finally, we have not been able to think of any mechanism other than the one under consideration which will produce in a given time a quantity of $C^{14}H_3NH_2$ depending only on the extent of double-labeling in the ethane, and independent of all other factors, e.g., the total amount of C^{14} in the system.

One point, however, remains to be resolved. Granted that the $C^{14}H_3NH_2$ originates in the decay of $C^{14}H_3C^{14}H_3$, is this methyl amine molecule the original entity, except as transmuted by beta decay; or, was it formed by the attack of a N^{14} fragment, which has torn loose from its parent, on another ethane molecule to reform $C^{14}H_3NH_2$? The question of "original retention" *versus* reformation is a vexing one in the whole field of hot chemistry. It is readily shown that if the distribution of C^{14} in the ethane is random the yield of $C^{14}H_3NH_2$ by the reformation process would vary with the fraction of C^{14} in the sample in the same manner as would the yield by "original retention." Therefore in most of our experiments the two effects would be indistinguishable. However in run $B-e$ the hot ethane was diluted approximately sixfold with inactive ethane during the growing-in period. This should decrease the yield of any $C^{14}H_3NH_2$ produced by reformation by the same factor. Since no change was observed it is concluded that reformation can be excluded as a source of $C^{14}H_3NH_2$. As this work was carried out in the gas phase the result is to be expected; however in the condensed phase this approach to the problem of retention could resolve a real ambiguity.

We may briefly consider several kinds of disturbances due to beta decay in a molecule, and how these might affect the yield of $C^{14}H_3NH_2$ in our experiments. The main effects to consider are: ionization due to direct interaction of the beta particle with an orbital electron; ionization or excitation due to the abrupt change in nuclear charge; recoil due to the emitted beta particle and neutrino; collisions subsequent to beta emission. These effects are of course not independent of each other but for the purposes of this discussion they will be treated separately. A more exact treatment of the first three of these effects on a C-N molecule is given elsewhere.[4]

As to direct ionization by the departing beta particle, one can expect from the specific ionization caused by electrons in air that this is not an important effect.[12] This expectation is confirmed by the result of Wexler and Davies[13] that the positive charge remaining after beta emission from C^{14} is unity, i.e., no orbital electrons have been lost. The same observation shows that ionization is not an important consequence of the increase in binding energy of the electrons when Z increases by unity.

The change in atomic number on beta decay involves the rearrangement of the orbital electrons to a new electronic configuration. When the nuclear charge increases, the binding of the electrons to the nucleus is strengthened and a corresponding amount of binding energy is made available. Were the emission of the beta particle an adiabatic process allowing continuous reestablishment of equilibrium, then the β^- particle would carry away all this excess binding energy leaving the system nonexcited. However the C^{14} beta particle is usually emitted at a velocity much larger than that of the orbital electrons. Serber and Snyder[14] have discussed nonadiabatic processes of this type and find that although the beta particle still carries away most of the excess binding energy, some will be left as excitation energy of the resulting system. The residual energy

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[12] See also remarks by H. Schwartz, J. Chem. Phys. **21**, 45 (1953).
[13] S. Wexler and T. H. Davies, Phys. Rev. **88**, 1203 (1952).
[14] R. Serber and H. S. Snyder, Phys. Rev. **87**, 152 (1952).

amounts to an average of about 45 ev for $C^{14} \to N^{14}$ decay. Although classically this would make molecular disruption almost inevitable, application of quantum considerations[4] shows that the probability distribution for depositing energy in the molecule in this way is highly skewed. Hence it seems entirely plausible that in most cases the molecular entity may survive the readjustment following the change in nuclear charge.

Simple calculations show that the recoil of a 0.155 Mev beta particle will impart a recoil kinetic energy of 7.0 ev to an isolated N^{14} atom. Similarly, the recoil of a 0.155 Mev neutrino will give a recoil energy of 0.9 ev. Conservation of momentum considerations show that in a $C^{14}H_3N^{14}H_3{}^+$ molecule 59% of the recoil energy, or 4.1 ev and 0.5 ev, respectively, will go into internal motions of the molecule. The rest appears as translational energy of the center of mass. A recoil energy of 3.56 ev is required to supply an energy in vibration and rotation equal to the $C-N$ bond energy of 2.1 ev.[15] This corresponds to the emission of a beta particle of 0.08 Mev. From inspection of the beta spectrum[16] of C^{14} one concludes that in about 80% of the decay processes the beta particle has less than this energy. (76% is calculated by Wolfsberg.[4])

If the $CH_3NH_3{}^+$ molecule has survived the effects just described, it will still have translational energy, in excess over that corresponding to thermal motions in the gas. The excess will range from a few tenths of a volt to about 2 ev. It is conceivable that on collision with another body this energy will be redistributed in such a way as to cause dissociation. The usual condition for low probability of interconversion of translational and vibrational energy,[17] namely that the "collision time" be large compared to the period of the vibration excited, may not be strongly satisfied here. However,

limitations on the energy transfer placed by conservation of momentum requirements appear to be sufficient to make dissociation of the $CH_3NH_3{}^+$ by collision improbable.[18]

Finally, the neutralization of the $CH_3NH_3{}^+$ molecule needs to be considered, although the present experiments do not bear directly on this question. Energetic considerations rule out charge transfer in a collision with an ethane molecule, and it may be supposed that the $CH_3NH_3{}^+$ loses its excess kinetic energy in such collisions before its charge becomes neutralized. Neutralization of the thermalized ion may occur either by reaction with a free negative charge, in which case survival of the CH_3NH_2 entity is not assumed; or by simple abstraction of the extra proton by a nucleophilic group in the gas or (as seems more likely) on the wall of the bulb. It may also be possible for the $CH_3NH_3{}^+$ molecule to lose H_2, giving $CH_2NH_2{}^+$, which subsequently gains a hydrogen atom and an electron.

The 47% retention of molecular integrity observed seems qualitatively consistent with the above sequence of events following beta decay. Detailed calculations[4] on the effects of change of Z and of the recoil do indeed lead one to expect about $60\pm20\%$. We believe that, in the case studied, the question of bond dissociation *versus* nondissociation in beta decay has been answered experimentally and is understood from the theoretical point of view.

ACKNOWLEDGMENTS

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[15] L. Pauling, *The Nature of the Chemical Bond* (Cornell University Press, Ithaca, 1948).

[16] S. D. Warshaw, Phys. Rev. **80**, 111 (1950).

[17] See, e.g., H. S. W. Massey and E. H. S. Burhop, *Electronic and Ionic Impact Phenomena* (Oxford University Press, New York, 1952), p. 454.

[18] Consider, for example, a completely inelastic collision between an initially stationary C_2H_6 and a $CH_3NH_3{}^+$ of kinetic energy T and vibrational excitation U. If the available energy is equally shared by the two molecules the excitation of each after collision will be $T/4+U/2$. In the energy range of interest there will be a net de-excitation of the hot molecule.