Chemical Forms Assumed by C14 Produced by Neutron Irradiation of Nitrogenous Substances

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Chemical Forms Assumed by C^{14} Produced by Neutron Irradiation of Nitrogenous Substances

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The nature of the radioactive compounds formed in the production of C^{14} by neutron irradiation of nitrogen-containing material of various types has been investigated. Of the radioactive compounds sought, carbon dioxide and carbon monoxide were found in all samples which contained oxygen, either in the parent compound or in the solvent water. Formic acid and methanol were found only in water solutions. Hydrogen cyanide, on the other hand, was found in no solution, but was found in all the pure substance samples except ammonium nitrate and aniline. Methane was found only in those hydrogenous substances containing no oxygen. Formaldehyde was never found. An attempt is made to interpret the results in terms of the processes in which the C^{14} atoms must be involved in the dissipation of the recoil energy associated with their formation. The fact that several compounds are produced in radioactive form in the original irradiation eliminates the necessity for the synthesis from radioactive carbon dioxide of these compounds for use in tracer work. A simplified method for the preparation of C^{14} is suggested.

AS an extension of the work of Ruben and Kamen[2] on the long-lived radioactive isotope of carbon, C^{14}, we have made chemical fractionations of the C^{14} radioactivity induced by neutron irradiation of several nitrogen-containing compounds of different types with a view to obtaining more detailed information as to the chemical form in which the newly created atom is to be found in a particular case and how this varies with the nature of the material irradiated.

The nuclear reaction involved is

$$_0n^1 + _7N^{14} = _6C^{14} + _1H^1 + Q,$$
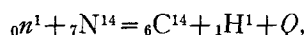
where Q has been estimated at about 0.60 Mev.[2,3] The C^{14} nucleus, therefore, acquires a recoil energy of approximately 40,000 ev, far more than enough to rupture any chemical bonds by which the nitrogen atom involved may have been held. The subsequent chemical fate of such an energetic atom is, in itself, a matter of interest, besides being, in the case of C^{14}, a matter of some practical importance.

Rather similar phenomena have been investigated[4] in the cases of several n, γ reactions and nuclear isomeric transitions which similarly yield excited monatomic products. One would expect that, after dissipation of their energy, these product atoms might appear in a new chemical species, in a substitution product of the parent compound, or even in molecules of the parent compound itself. All three possibilities have been realized and attempts have been made to correlate and interpret the results, but few generalizations have been possible. The work has been particularly fruitful, however, in suggesting methods to be used in extracting the induced activity from the irradiated material.

We too have tried to explain our results: certain plausible and interesting correlations have been found possible. The work has potential value, moreover, as an aid in the preparation of C^{14} for use as a tracer, in which connection it was originally undertaken. With a neutron source such as the Berkeley cyclotron, this isotope, because of its long half-life, can be obtained in only small yields, with low specific activities, and these only with considerable labor. Our data are helpful in suggesting the most efficient and least tedious methods of extracting and concentrating the isotope from the bulk of irradiated material.

We hope, moreover, that the information may be useful in another connection as well. One of the principle hindrances to the use of C^{14} as a tracer in research in organic chemistry or the life sciences is the difficulty involved in its incorpora-

[1] From a dissertation submitted in partial satisfaction of the requirements for the degree of Doctor of Philosophy.

[2] S. Ruben and M. D. Kamen, Phys. Rev. **57**, 549 (1940); **59**, 349 (1941).

[3] T. W. Bonner and W. M. Brubaker, Phys. Rev. **49**, 223 (1936).

[4] Szilard and Chalmers, Nature **134**, 462 (1934), and many other workers. For a review see G. T. Seaborg, Chem. Rev. **27**, 199 (1940).

tion into various organic compounds. One must have available a semi-micro synthetic method which uses carbon dioxide as a starting material and produces good yields (usually 50 percent or better) without undue dilution of the radio-activity. Such a situation exists for only a limited number of simple compounds. The possibility of placing the C^{14} in a particular desired compound in the first place, simultaneously with the original production of the radioactivity, cannot fail to be attractive; it was hoped that this work might be suggestive along this line.

In addition to the samples we fractionated, several others were irradiated, but, because of their small size, these failed to accumulate sufficient radioactivity to be handled. Much desirable additional data is, therefore, not yet available.

EXPERIMENTAL

Samples

Three groups of samples were subjected to irregular irradiation with neutrons from the Berkeley 60-inch cyclotron for a period of about two years. The irregularity precludes any estimate of total neutron dosage. However, since the groups were maintained intact for this period, the dosages and hence, roughly, the yields of C^{14} per gram of nitrogen should have been more or less comparable within a given group. As an examination of the data will show, this is borne out only very approximately by experiment. The discrepancy may arise in part from shielding of one sample by another. This should have been particularly true of the large samples in Group I.

Group I consisted of twenty-five stainless steel tanks, 15 to 30 liters in volume, filled with saturated ammonium nitrate solutions. Of these we analyzed only three tanks in detail.

Group II consisted of 500 g of ammonium nitrate crystals, 100 g of hydrazine dihydrochloride, and 330 g of dry aniline, all in sealed containers. The hydrazine contained about 2 percent moisture.

Group III was composed of 170 g of ammonium nitrate crystals, 210 g of urea crystals, a saturated solution of urea containing about 300 g of solute, and a 50 percent pyridine-water solution containing about 100 g of pyridine. The seals on all but the second of the samples in this group

were found to have been imperfect, resulting in loss of gaseous activity.

Fractionations

We adopted an analytical procedure designed to locate C^{14} activity present in the form of what seemed the most likely one-carbon compounds: carbon dioxide, carbon monoxide, methane, hydrogen cyanide, formaldehyde, methanol, and formic acid. It would have been of considerable interest to look for substitution compounds, which were, in all probability, formed in certain cases—a probability indicated by the low apparent yields of radio-carbon, particularly in the case of aniline—but the impracticality of extracting such compounds in view of the very low activities involved precluded this possibility.

With variations for the different cases, a more or less general procedure was followed, involving analysis of three fractions: gaseous activity in the gas phase over the sample; gaseous activity trapped within the sample; and non-volatile, water-soluble activity in the sample.

The first fraction, consisting of the activity in the gas phase over the sample, was isolated by connecting the sample vessel to a large evacuated bulb and allowing the pressure to equalize between the two. The large bulb was then shut off, and the sample container allowed to fill with air. The two vessels were again connected and the pressure allowed to equalize. This procedure was repeated until the pressure in the large bulb had reached almost an atmosphere. This bulb, to which 4.2 cc each of carbon dioxide, carbon monoxide, and methane had previously been added as carriers, was now connected to an analytical train, and its contents were swept through the train with oxygen at a rate of 5 to 10 liters per hour. In this train, the gases passed first through a bubbler containing dilute sodium hydroxide, by which the carbon dioxide was removed, then through a copper oxide combustion tube at 315°C in which carbon monoxide was oxidized to carbon dioxide, through another bubbler to absorb this gas, through a second copper oxide tube at 700°C to oxidize methane, and through a final bubbler to absorb the carbon dioxide from this oxidation. Barium carbonate was precipitated from the three alkaline solutions and "counted" as such. This procedure was found

quantitative in blank experiments at the flow rate given.

To separate the second and the third fractions, the solution of the sample (if a solid, it was first dissolved) was acidified with nitric acid, shaken with 4.2 cc each of carbon dioxide, carbon monoxide, and methane, and then aerated with oxygen for a long period, the gas stream being passed through the same analytical train as before. This constituted the second fraction; the third fraction remained in the out-gassed solution, which was then neutralized preparatory to treatment.

This solution containing the third fraction was first examined for radioactive cyanide. To the whole, or an aliquot, one millimole of potassium cyanide carrier was added and then precipitated as silver cyanide. The solution was maintained at 0°C for two hours before filtration. The solid silver cyanide was counted as such. In the cases of the hydrazine, the glycine, the aniline, and the pyridine, this procedure proved unsatisfactory, so chloride ion, if not already present, was added, and a mixed precipitate of silver chloride and silver cyanide was obtained. This precipitate was crushed up thoroughly in water, the suspension made $0.1N$ in sodium hydroxide, and excess potassium permanganate added. Thirty minutes of boiling sufficed for complete oxidation of the cyanide to cyanate, while leaving the chloride unaffected. After destruction of excess permanganate as described below, acidification resulted in hydrolysis of the cyanate to ammonium ion and carbon dioxide, and the latter was then swept out of the solution with a stream of oxygen, absorbed in sodium hydroxide, and precipitated and counted as barium carbonate.

To the filtrate from the cyanide separation was next added a small quantity each of formaldehyde, methanol, and formic acid. The solution was acidified and these compounds separated from the bulk of the original material by distillation of the solution as nearly to dryness as seemed practical. Formaldehyde was separated from the distillate by precipitation as the 2,4-dinitrophenylhydrazone. The distillate was then made alkaline and again distilled down to one-fifth its original volume. The residue contained the formate and the distillate the alcohol. These solutions were made $0.1N$ in sodium hydroxide,

excess potassium permanganate was added, and the two compounds were oxidized to carbonate by three minutes of boiling. Excess permanganate was destroyed by dropwise addition of potassium iodide to the solutions to which excess ammonium chloride had also been added, and then, after acidification, carbon dioxide was swept out and converted to barium carbonate for counting.

This was the general procedure followed with all the samples. Certain necessary variations made may be noted. In the cases of three of the samples, the containers were imperfectly sealed and the results for gaseous activities in these instances were consequently of questionable validity. With the urea solution, for this reason, the first and second fractions were combined before analysis. In the case of the aniline, it was convenient for other experimental reasons to do likewise. Moreover, this substance is, of course, not miscible with water, so the procedure for fraction 3 had to be modified. Water-soluble activity was extracted with successive portions of dilute sodium hydroxide containing carrier cyanide, followed by dilute hydrochloric acid, then more base and finally water. These water solutions were combined and silver cyanide and chloride were precipitated and treated as described before. The filtrate was subjected to oxidation by alkaline permanganate and the barium carbonate thus obtained counted as "other water-soluble activity." Finally, in the case of the pyridine, concentrated sulfuric acid was added prior to the distillation of the formaldehyde, methanol, and formic acid from the sample to prevent volatilization of the pyridine itself.

Counting

In this work we have adopted a more satisfactory method for measuring the radioactivity than has hitherto been used for C^{14} in this laboratory. Because of the low energy ($145,000\pm15$ ev^2) of its beta-particles, this isotope has, until now, been counted either as a thin layer of solid, e.g., barium carbonate, mounted inside a screen-wall counter[5] or as gaseous carbon dioxide directly introduced into a counter. Both of these methods have their disadvantages in loss of time and lack of accuracy. A rather similar problem exists in

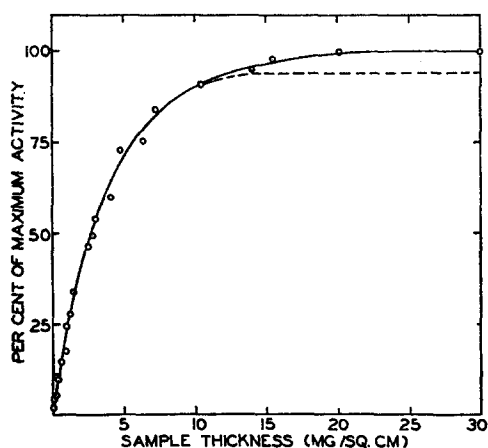[5] W. F. Libby, Phys. Rev. **46**, 196 (1934).

FIG. 1. Increase in apparent activity as increasing weights of a single $BaC^{14}O_3$ sample are counted. Broken line indicates divergence from our results of a curve calculated on the basis of the data of Ruben and Kamen (see reference 2).
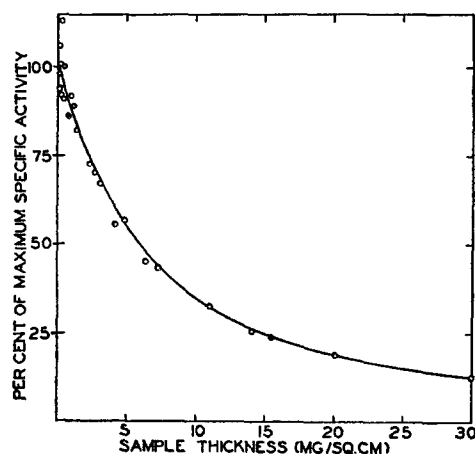

FIG. 2. Specific activity of a $BaC^{14}O_3$ sample *versus* sample thickness.

the case of S^{35}, the upper energy limit of whose beta-particles is 120,000 ev.[6] Workers with this isotope[7] have lately succeeded in counting it as a thin layer of barium sulfate placed just below the thin mica window of a bell-jar type counter, thus avoiding the necessity of refilling the counter tube for each sample. With certain variations, we have adopted their method for C^{14}.

Our counter tube consisted of a bell-jar shaped glass housing, containing a brass cathode and a central tungsten wire, and with a mica window at the bottom. The window was 3.0 mg/sq. cm in thickness, 60 mm in diameter, and was reinforced on the inside by a light-weight, open-mesh brass screen. The cathode, which was one centimeter above the window, was 5.0 cm long and 4.8 cm in diameter. A mixture of 740 mm of helium and 10 mm of ethanol, used as a filling gas in this work, performed satisfactorily. We have lately, however, been using the better argon and alcohol (90 mm and 10 mm) mixture in these counters, despite the difficulty of obtaining windows of sufficient strength to withstand the external pressure.

The samples were isolated as barium carbonate and, in two cases, silver cyanide and were counted as thin layers of these solids mounted on thin aluminum disks (weight about 0.6 g) placed two millimeters below the counter window. The

geometry was well standardized, so that reproducible results might be expected. The disks fitted snugly into a machined brass carriage which slipped into a fixed position under the counter. Background determinations were easily made by replacing the sample with a clean disk. (As might be expected, a disk mounted with inactive barium carbonate gave the same background count as a clean disk.) Accurate weighing of the samples was facilitated by the lightness of the disks. The samples were mounted by a technique similar to that used by Hendricks et al.[7] for barium sulfate. A brass cup with straight sides and a flat bottom was provided with a thick concentric sleeve fitting snugly inside of it and machined to give a good seal with the bottom when forced down by a screw arrangement. The aluminum disks were of such size as just to cover the bottom of the cup; thus, the sleeve, when inserted, would seal their edges. A suspension of the solid sample in 95 percent ethanol was placed in the cup, allowed to settle, and the excess alcohol evaporated off by gentle warming. The disks were then removed and weighed. The area of the mounted sample being known (11.6 sq. cm), an accurate estimate could be made of the thickness of the sample, which was necessary in order that a correction for self-absorption might be applied. For reproducibility, uniformity of sample layer was essential; our method of mounting gave this, except for very heavy layers (>20 mg/sq. cm), with which thin patches developed, giving an apparent enhance-

[6] M. Kamen, Phys. Rev. 46, 196 (1934).
[7] Hendricks, Bryner, Thomas, and Ivie, J. Phys. Chem. 47, 469 (1943).

ment of activity. In these cases, tamping the dried coating with the flattened end of a glass rod obviated this difficulty.

The self-absorption correction was experimentally determined by measuring the apparent activity of varying weights of a single radioactive barium carbonate sample mounted as described above. As expected, the activity at first increased with increase in size of the specimens, but eventually a maximum activity was obtained which could not be further increased.

The results are shown in Fig. 1, plotted as percent of this maximum activity vs. thickness of coating. The experimental curve coincides exactly with a curve calculated on the basis of Ruben and Kamen's[2] data on absorption by aluminum foil up to about 12 mg/sq. cm. The calculated curve (shown as a broken line) comes to a saturation value at 16 mg/sq. cm, however, and at a value about 6 percent below the experimental value. A plot of the percent of that activity which would be observed if the sample layer were of zero thickness is shown in Fig. 2,

based on the same data as Fig. 1. This figure enables one to make direct comparison between samples of various thicknesses; we used it to correct all our data to zero thickness. The corrections for silver cyanide were assumed the same as those for barium carbonate.

It would, of course, be quite convenient for work with this isotope if it were available in such quantities that samples of thickness greater than 25 mg/sq. cm only, for instance, might be counted, thus eliminating the necessity for any correction.

RESULTS

The experimental results are shown in Table I. The first column gives the sample fractionated; the group in which it was irradiated is indicated by the Roman numeral in parenthesis. The succeeding seven columns show the total activity in each fraction in counts per minute, in most cases computed from an actual count made on an aliquot of the whole fraction. For carbon dioxide, carbon monoxide, and methane the two figures

TABLE I. Fractional distribution of activity in the samples.

Sample	CO₂	CO	Activity in fractions (counts per minute) CH₄	HCN	HCHO	CH₃OH	HCOOH	Activity per g N
NH₄NO₃ Soln. (I)	3,300±150 62,800±2500 38.0%	71,500±5000 6600±400 44.8%	1700±100 2150±500 2.2%	0±60	0±100	1600±200 0.9%	24,700±2000 14.1%	38
Soln. (I)	42,300±600 315,000±7000 59.4%	166,800±4000 11,100±400 29.5%	450±80 0±50 0.1%	0±1000	0±100	8600±1000 1.4%	57,700±2500 9.6%	80
Soln. (I)	850±150 14,300±1000 16.5%	60,500±3000 11,700±400 78.5%	600±200 350±100 1.1%	0±150	0±120	3700±1000 4.0%	lost	13
Crystals, 170 g (III)ᵃ	0±10 450±50	0±10 185±25	0±10 0±10	0±10	0±10	0±20	0±20	10.6
Crystals, 500 g (II)	775±40 205±20 81.0%	160±25 70±10 19.0%	0±15 0±15	0±15	0±6	0±20	0±20	6.9
(NH₂)₂CO Soln. (III)ᵃ	0±10	0±10	0±10	0±20	0±10	110±30	455±50	4.0
Crystals (III)	215±15 140±20 39.5%	45±10 0±10 5.0%	0±6 0±15	500±100 55.5%	0±10	0±20	0±20	9.2
N₂H₄·2HCl Crystals (II)	77±15 0±7 17.8%	36±10 0±10 7.9%	19±5 0±10 4.2%	325±50 71.1%	0±10	0±20	0±20	17.1
NH₂CH₂COOH Crystals (II)	0±6 13±5 7.7%	0±6 0±4	0±10 0±8	25±8 14.9%	0±6	(80±20) 47.6%	(50±10) 29.8%	12
C₅H₅N Soln. (III)ᵃ	32±6	0±10	0±10	0±12	0±10	0±20	36±20	3.8
C₆H₅NH₂ Liquid (II)	0±6	0±10	41±6	0±12	0±50			.82

ᵃ Containers were imperfectly sealed.

given represent, respectively, gas phase activity and activity trapped within the sample—solution or crystals as the case may be. The percentages shown indicate the portion of the total activity which the particular fraction represents. The last column gives the total activity isolated divided by the grams of nitrogen in the sample, and, as mentioned before, these figures should be more or less the same within each group. The limits of error shown represent "presumable errors," in most cases somewhat larger than "probable errors" computed on the basis solely of statistical fluctuation of the radioactive decay. They attempt to take into account other, often greater, sources of error, such as variability in counter behavior, non-uniformity of the mounted samples, etc. The use of calculated "probable errors" for these data cannot fail to be misleading. It will be observed that the magnitude of these errors shows a large variation. This arises from the fact that aliquots counted represented very much smaller percentages of the total fraction in some cases than in others. Where an aliquot of a bulky fraction showed little or no activity, the error became quite large.

The data for some of the samples require a certain amount of explanation and amplification.

Ammonium Nitrate Samples

In the saturated ammonium nitrate solutions, methane activity is irregular, varying from zero to about 2 percent; it is, moreover, irregularly distributed between solution and gas phase. We suspect this activity to be apparent only, appearing as a result of incomplete oxidation of carbon monoxide in the first combustion tube, so that a certain amount of the activity associated with it was not absorbed by the alkali, but carried over into the methane fraction. This belief is based in particular on the case of the first ammonium nitrate solution, which shows the highest apparent methane activity. After completion of the analysis of this solution, it was found that gas flow rates through the analytical train of 20 and 26 liters per hour had been used inadvertently for gas phase activity (fraction I) and dissolved gaseous activity (fraction II), respectively; preliminary experiments had shown a rate of 5 to 10 liters per hour to be satisfactory. A check on the weights of barium carbonate obtained for the carbon monoxide and methane fractions from fraction II indicated that the latter was larger, and the former smaller than the known amounts of "carriers" which had been added by approximately the right amount to account for all the apparent radio-methane. Although lower gas flow rates were subsequently used, it seems quite reasonable to suppose that the small amounts of "radio-methane" found in the other ammonium nitrate solutions are to be accounted for in a similar fashion. Methane should, therefore, probably be considered inactive.

In addition to the compounds shown, radio-carbon in the elemental state was a possibility, although an unlikely one. It was not experimentally practical to look for it on the walls of the tanks, where there might have been the best possibility of finding it, but it was shown to be absent in the solution, a sample of which was filtered several times through a bed of graphite. This graphite, after washing with acid to remove any carbonate, was found inactive.

It is evident that the proportions of carbon monoxide, methanol, and formic acid are roughly the same for the three solutions, which is what might be expected. The percentages of carbon dioxide, however, vary erratically. This is, we think, caused by the fact that there was a good deal of iron rust (from pipe fittings) inside the tanks. The rust was found to be slightly active, presumably as a result of reacting with some of the active carbon dioxide. The distributions of the radioactive gases between the gas phase and solution are interesting to examine in this connection. Knowing the solution and gas space volumes, one may calculate from the observed activity distribution a distribution coefficient for equal volumes. Computed as gas/liquid activity, the values for carbon monoxide are 84, 93, and 73 for the three cases. These compare favorably with an expected value of about 86.[8] For carbon dioxide the values 0.55, 0.83, and 0.84 are obtained, which are to be compared with an expected value of about 2.5.[9] That the carbon dioxide had not become equilibrated between the two phases seems unlikely in view of the carbon

[8] From Winkler, Ber. **34**, 1408 (1901), a distribution coefficient for water at 20°C of 43 is obtained. By analogy with other cases this should be approximately doubled for saturated ammonium nitrate.

[9] Setschenov, Ann. de Chimie [6] **25**, 226 (1892).

monoxide result and the fact that the tanks stood for about eighteen months between the end of their irradiation and their analysis. Rather the preferential absorption by the rust of the gas phase carbon dioxide seems the best explanation. Thus, too, could the wide discrepancy between the three yields shown in the last column be accounted for—although, as mentioned before, this may be explained in part as resulting from shielding of one tank by another.

In the case of the ammonium nitrate crystals, the absence of activity in the gas phase over the 170-g sample is to be ascribed to loss from an imperfectly sealed container. However, the fact that the yield of C^{14} is the greatest for this sample of all those in Group III suggests that this loss was not too large; i.e., most of the activity must have been trapped in the crystals. Yet with the 500-g sample the bulk of the activity was found in the gas phase. These results can perhaps be reconciled by the fact that the crystals of the 170-g sample were considerably coarser than those of the 500-g sample. The much greater surface in the latter case might have resulted in diffusion into the gas space of considerable activity trapped immediately below the surface. It is interesting to note that in these samples there is two to four times as much active carbon dioxide as carbon monoxide, a result not inconsistent with the solution results.

It might be noted that these results amplify those of Ruben and Kamen[1] in that the latter found only gaseous activity in the ammonium nitrate solutions and no gas phase activity over the crystals

Other Samples

The fact that carbon dioxide and carbon monoxide are formed with urea crystals, and that they were found in the ammonium nitrate solutions as well as crystals, suggests that they were also formed in the urea solution. Their absence presumably results from the fact that the container was poorly sealed. We suspect their loss from the badly sealed pyridine solution as well, the small carbon dioxide activity representing only a residue. The appearance of oxygen-containing activity in the hydrazine doubtless results from the fact that the crystals were moist. The presence of this activity in the gas phase only

is consistent with this idea. In the case of the glycine, the formic acid activity shown must be taken as a lower limit, since it represents a measurement made on only a portion of the formic acid fraction. The barium carbonate from the remainder became so diluted with inactive barium carbonate resulting from decomposition, in the course of the analysis, of the glycine itself that measurement of the activity of this portion became impossible. In regard to this glycine, it is quite possible that the activity given for methanol and formic acid does not actually belong to these compounds. Our analytical scheme distinguished only between alcohols, acids, and aldehydes. For most of the samples irradiated, the absence of carbon chains made improbable the formation within these classes of any compounds other than methanol, formic acid, and formaldehyde. A glycine molecule could, on the other hand, have reacted with a radioactive carbon atom to produce 2- or 3-carbon compounds, and any of these which were alcohols or acids would have appeared in our scheme as methanol and formic acid.

DISCUSSION

Certain facts in regard to the type of environment favorable to the formation of each of the carbon-containing compounds are immediately apparent from our results; others, while not so obvious, may be inferred.

Carbon dioxide and carbon monoxide are produced in the irradiation of all oxygen-containing material, except glycine where, although there is no apparent carbon monoxide, the expected amount would probably be within experimental error; these gases were presumably lost by leakage from the urea and pyridine solutions. Carbon dioxide tends to appear in considerably greater abundance than carbon monoxide (see above for discussion of disappearance of carbon dioxide from the ammonium nitrate solutions) and these substances together tend to contain the bulk of the activity, except where there exists a good possibility for the formation of addition or substitution compounds with the parent substance, such as in the cases of glycine or pyridine.

Methane, it may be seen, appears only in the absence of oxygen and in the presence of a relatively high hydrogen density (see above in regard to the ammonium nitrate solutions).

Hydrogen cyanide is to be found in the absence of water and of a high oxygen concentration. Formaldehyde formation does not appear to be favored by any of the conditions covered by this work. Methanol and formic acid tend to appear together in the presence of water, the latter in considerably greater abundance.

In the irradiation of the more complicated compounds, glycine, pyridine, and aniline, it is evident that most of the activity has not been properly accounted for. We had originally planned more elaborate fractionations of these substances, but their total C^{14} content did not make such feasible.

The question may be raised as to the influence on the results of thermal exchange reactions, occurring over the long period of time involved in the irradiations. For instance, since, in all solutions, inactive carbon dioxide impurity was undoubtedly large compared to carbon monoxide impurity, an exchange reaction would tend to produce an equilibrium condition in which the bulk of the carbon monoxide activity would have been transferred to carbon dioxide. Although such reactions may perhaps be excluded by the argument given below for thermal reactions in general, they may probably equally well be excluded in most cases solely on the basis of improbability. The exchange mentioned, between carbon dioxide and carbon monoxide, for instance, is known to occur, in the gas phase, at an appreciable rate only at temperatures in the region of 800°C;[10] one may perhaps reasonably infer from this that the occurrence of the exchange in our solutions at a measurable rate at room temperature is unlikely. A detailed examination of other possibilities for exchange which might influence the distribution of the activity suggests that in general they would require a high activation energy and consequently may be considered improbable. We have, therefore, disregarded reactions of this type in the interpretation of our results.

It is interesting to attempt an explanation of the results in terms of the processes in which the C^{14} atoms must be involved immediately after their formation. These atoms are, as mentioned

before, more than assured of ejection from any parent molecule by virtue of the recoil energy, ~40,000 ev, associated with their formation, and will, consequently, first appear as swiftly moving single atoms. We say atoms, not nuclei, inasmuch as the particles will probably never be stripped of all their electrons, since the velocity associated with the recoil energy, ~7.4×10^7 cm/sec., is that of an electron of only 1.6 volts. The question is, now, what will become of such atoms. Their behavior will, in all probability, be rather like that of α-particles which have become reduced to comparable energies. Their kinetic energy will doubtless be dissipated in a succession of collisions with the atoms and molecules of the environment, these collisions leading to a good deal of ionization and radical formation. In this process the particles will travel a considerable distance from the locale of their birth. Along their paths they will probably, by analogy with α-particles, change charge a large number of times, but the predominating tendency will be to gain electrons. Only toward the end of the paths, after most of their initial energy has become dissipated, will there exist a reasonable probability of formation of combinations with other atoms. It seems reasonable to suppose that these first combinations should be diatomic and that the nature of the partner atoms should be more or less randomly determined by the relative abundance of the different atomic species in the medium. A particular combination may or may not be a potentially stable one; it may carry a charge or be a radical. Most important, it will still be quite energetic and will tend to undergo further "high energy" reactions on collision with other molecules. It may add further atoms; it may exchange "partner atoms;" it may change its charge; it may be broken up.

These first reactions may not necessarily lead to a more stable combination. However, the energy level will soon drop below that required for the "high energy" reactions, leaving the radioactive substance, whatever may then be its form, in a state analogous to chemical activation. In this state, it will tend to undergo only reactions which result in a decrease in free energy, i.e., those leading to relatively stable molecules. It seems reasonable to suppose that at this stage most of the radioactive atoms will reach a stable

[10] J. D. Brandner and H. C. Urey, J. Chem. Phys. **13**, 351 (1945).

form and so remain. Free radicals or unstable ions reaching room temperature should still be quite reactive and should soon react to produce stable radioactive compounds. The predominance of relatively stable compounds among the products shown in Table I lends support to these ideas. We suggest, therefore, that thermal reactions occurring over a period of time subsequent to the recoil process will not be important in determining the final chemical form of the radioactivity: almost all such reactions will have occurred toward the end of the recoil process itself.

Let us now see how the experimental results fit into the picture just outlined.

In the ammonium nitrate solutions the first combinations must obviously be with hydrogen, oxygen, or nitrogen, in that order of probability. A C$-$H combination should be quite unstable and should soon change to one of the other forms or else add another atom, the most probable being another hydrogen, thus giving an excited methylene. This methylene will then either be oxidized to carbon monoxide or carbon dioxide or else become hydrated: thus the formation of methanol is explained. The lack of formation of methane, or at least the very low incidence of it, is easily explained on the basis of the low probability of the addition of two more hydrogens to the methylene, compared to the probability either of oxidation or of hydration. In like manner the absence of formaldehyde may be accounted for. This would most readily be formed by the addition of an oxygen to methylene, but the probability of this process should be low compared to that of the hydration process. The C$-$O combinations which survive the "high energy" reaction stage may either dissipate their remaining energy, and settle down as normal carbon monoxide molecules, or, in consequence of the high concentration of nitrate ions in a somewhat acid medium may, while excited, be oxidized to carbon dioxide molecules, which then remain as such. The data indicate the higher probability of the latter event, a not unexpected result. The C$-$N combinations might perhaps be expected to lead to formation of stable hydrogen cyanide; the fact that this compound is not formed may possibly be explained by either of two occurrences. The cyanide while still excited

will have a strong tendency toward oxidation to cyanate. This, in the acid medium prevailing, would at once be hydrolyzed. Failing this event, the tendency of hydrogen cyanide toward hydrolysis might lead to the rapid conversion of the radio-cyanide to ammonium formate. The latter alternative would explain nicely the absence of cyanide coupled with the presence of a large amount of formate. In regard to the possible relative importance of the first suggestion, however, our data can give no information, since the radioactive carbon dioxide which would be formed thereby would be indistinguishable from that formed by other mechanisms.

In the case of the ammonium nitrate crystals, there is still a high concentration of oxygen, and as might be expected the two oxides of carbon are formed in large amounts. The CO_2/CO ratio is even larger for the crystals than for the solutions. This may be explained either by the post-irradiation loss of carbon dioxide from the solutions, as already discussed, or by the fact that the solid is probably a stronger oxidizing medium than the solution. As with the solution, no methane is formed, and the explanation of this is doubtless to be found in the high probability of oxidation of methylene, even if formed, in such a medium. The absence of water accounts for the non-formation of methanol. Lacking the possibility of hydration, the methylene presumably is oxidized. One might anticipate the formation of formaldehyde under these circumstances. It is evident from its absence that the oxidation of methylene proceeds beyond the stage of this compound. It is interesting that no cyanide appears in this case. This is most easily explained by supposing that any C$-$N intermediates are oxidized to cyanate. This substance would, of course, hydrolyze to carbon dioxide and ammonium ion on solution of the crystals in an acid medium. The fact that no formate is to be found is in line with our suggestion that this is formed through the reaction of a not quite de-energized cyanide with the water in the solution.

The first instance of cyanide formation is that of the urea crystals. Here there exists a relatively greater concentration of nitrogen and smaller concentration of oxygen, so the C$-$N combinations should have a strong tendency toward formation and but a slight one toward oxidation

to cyanate. The non-formation of formate is again to be explained by the absence of water. Carbon dioxide and carbon monoxide are formed, but in much smaller amounts, because of the low concentration of oxygen. Water being absent, methanol is not formed; and methane is again absent because of the improbability of the acquisition by methylene of two additional hydrogens. Comparing with these results those for the solution of urea, we find just the expected changes in distribution of activity. The cyanide disappears and a roughly comparable quantity of formate appears. (The solution and solid contained, respectively, about 300 g and 210 g of urea, and the yields should have been approximately the same since both samples were in Group III.) Methanol again makes its appearance, presumably as a result of the presence of water.

Consequent to the high concentration of nitrogen and the absence of oxygen in the hydrazine, cyanide is the chief product. This activity was presumably trapped within the crystals and despite the small amount of moisture present, no formate was formed. Because of the considerable tendency toward their formation, however, the two oxides of carbon did appear possibly as a result of the presence of the water. The concentration of oxygen in the air within the sample container would not seem sufficient to account for the formation of these compounds (cf. their non-formation in the case of aniline). In this case also, the high hydrogen concentration and absence of oxygen made possible the production of a small amount of methane.

It is evident that the formation of cyanide in the case of the glycine crystals and its non-formation coupled with the appearance of formate in that of the pyridine solution is consistent with our picture. The appearance of methane in the aniline of course results from the absence of oxygen coupled with a high hydrogen concentration.

The foregoing discussion gives a reasonable and self-consistent explanation of our experimental results. Our data cannot be considered sufficiently extensive, of course, to preclude the possibility of an alternative picture. With the neutron sources now available, it should not be difficult to extend our data considerably.

Practical Considerations

In regard to the possibility, mentioned in the introduction, of "on the spot" syntheses, it is evident that a proper choice of material to be irradiated may lead to the production of any one of several desirable C^{14}-containing compound. Radio-cyanide is relatively easy to obtain synthetically from carbon dioxide, but its direct production would obviate the necessity for this operation. Methanol is more difficult to prepare synthetically; it could be quite easily concentrated from the irradiated solutions. Formic acid also might be of considerable value in tracer work. More complicated compounds are doubtless formed in the cases of glycine, pyridine, and aniline, but no definite conclusions can be drawn from our data.

It is also evident from this work that, in the preparation of C^{14} by irradiation of ammonium nitrate with neutrons, the task of separating the activity could be greatly simplified if one were to use a saturated solution in a closed container with an adequate gas space over the solution. The bulk of the activity (in the form of carbon dioxide and carbon monoxide[11]) could be simply pumped off periodically, thus doing away with the laborious task of handling the solution itself. Methanol and formic acid would, of course, accumulate in the solution and, if desired, these could eventually be recovered.

[11] If we assume the addition of no carriers, the carbon monoxide can normally be isolated with a very much higher specific activity than the carbon dioxide, since the latter invariably becomes diluted with inactive atmospheric carbon dioxide.