[CONTRIBUTION FROM THE NOYES LABORATORY OF CHEMISTRY, UNIVERSITY OF ILLINOIS]

Chemical Forms Assumed by C^{14} Produced by Pile Neutron Irradiation of Ammonium Bromide: Target Dissolved in Water

BY PETER E. YANKWICH AND J. D. VAUGHAN

RECEIVED SEPTEMBER 23, 1954

Chemical fractionations have been made of the radiocarbon activities produced when pile neutron-irradiated ammonium bromide crystals are dissolved in water. Methylamine is formed in greatest amount (80% of the total activity); other radio compounds found are methane (7.5%), formaldehyde (6%), cyanide (2%), and methyl bromide, carbon dioxide, carbon monoxide, formic acid, methanol and urea (each less than 2%). The paths leading from possible crystal-stabilized conglomerates to final post-solution products are explored.

The C^{14} particle resulting from the transformation $N^{14}(n,p)C^{14}$ carries some 40,000 e.v. from the site of the nuclear event. This energy is dissipated to the surroundings by collision, ionization, etc., and stable chemical combination of the C^{14} with fragments from the disturbed environment is possible only when the energy of the recoil particle has fallen to, say, 100 e.v. or less. When the C^{14} has been thermalized, its state may be stable toward destruction of the parent crystal by solvent action, or such that reaction with the solvent takes place rapidly. Thus, it seems likely that determination of the distribution of radiocarbon produced over various terminal forms will yield information concerning the state of C^{14} in the original target crystals. To this end, and as an extension of earlier work,[1,2] we have made chemical fractionations of the carbon fourteen activities produced when samples of pile neutron-irradiated crystalline ammonium bromide are dissolved in water. In the study reported here an attempt has been made to account for essentially all of the radiocarbon produced. This goal has necessitated the development, proof and use of rather involved analytical procedures.

Experimental

Sample Preparation and Irradiation.—Twenty grams of reagent grade crystalline ammonium bromide was dried for two hours at 110°, then placed in a quartz tube which was stoppered with a perforated cork (to permit escape of hydrogen or other gaseous evolute during the irradiation), and the whole enveloped in Parafilm to exclude air.[3] Irradiation was carried out at the Argonne National Laboratory; pertinent data are: neutron flux, about 10^{12} cm.$^{-2}$ sec.$^{-1}$; X-ray and γ-ray flux, 530 R. min.$^{-1}$; sample temperature, 36°; irradiation time, 1172 hours. The sample was allowed to cool off for six months following irradiation, then transferred to an ordinary weighing bottle; from that time, the crystals were in contact with air.[4]

Preliminary Experiments.—In order to establish approximately the distribution of carbon radioactivity among the several species likely to result when a portion of the target material was dissolved in water, solutions of the irradiated ammonium bromide were subjected to analysis for carbon dioxide, carbon monoxide, methane, cyanide, formate, formaldehyde, methanol and basic compounds (represented by methylamine).

The solution apparatus consisted of a 70-ml. pear-shaped flask to which was fitted a cap which carried a fritted glass bubbler tube, several pressure-compensated funnels for the addition of solvent or carrier and reagent solutions, and a sweep gas outlet. A small amount (0.221 and 0.635 g., respectively, for the two preliminary runs) of target was weighed into the flask, then dissolved in 15–20 ml. of freshly distilled water. When the ammonium bromide had dissolved, acidic solutions of the various carriers were added from other funnels[5]; the final solution volume was 50–60 ml.

Through the solution was swept dry, carbon dioxide-free air. At the beginning, the sweep entered the solution vessel through gas burets containing 1 millimole each of carbon dioxide, carbon monoxide and methane. As the sweep left the dissolver it passed into an analytical train consisting of: (i) an absorber filled with aqueous sodium hydroxide for removal of carbon dioxide; (ii) a U-tube, held at room temperature, packed with Hopcalite[6] for oxidation of carbon monoxide[7] to the dioxide (after 15 minutes sweep, the U-tube was heated to 140° in an oil-bath so that adsorbed carbon dioxide would be released); (iii) a second sodium hydroxide-filled absorber for removal of carbon dioxide due to original carbon monoxide; (iv) a Vycor furnace tube packed with copper oxide wire, heated to 700–750°, for oxidation of methane; (v) a third sodium hydroxide-filled absorber for removal of carbon dioxide due to original methane.

To the degassed solution containing the carriers for the non-gaseous compounds was added excess aqueous silver nitrate and, after a few minutes stirring, a slight excess of saturated aqueous sodium chloride. The silver cyanide–chloride–bromide precipitate was removed by filtration, washed with water, then treated with boiling alkaline permanganate.

The filtrate from the cyanide precipitation was brought to 100 ml. total volume and a 25-ml. aliquot removed for determination of total non-gaseous activity (TNG)[8]; alkaline permanganate oxidation served to convert all carriers to carbonate. A second aliquot (50 and 25 ml., respectively, in the two preliminary runs) was taken for determination of the individual non-gaseous carrier activities, each fraction isolated being treated with alkaline permanganate.

The second aliquot was distilled almost to dryness; the residue was taken as a total basic fraction, methylamine hydrochloride being the effective carrier. The distillate, containing formic acid, formaldehyde and methanol carriers, was neutralized with carbonate-free sodium hydroxide, then buffered at *p*H 10 by the addition of boric acid and dilute sodium hydroxide; this solution was then distilled almost to dryness.[9] The residue contained the formic acid carried as its sodium salt. The distillate was made about 0.3 *M* in base, 5 ml. of 30% hydrogen peroxide was added, and the whole allowed to stand for 2 hours, after which time it was distilled almost to dryness. The residue from this third

---

[1] P. E. Yankwich, G. K. Rollefson and T. H. Norris, *J. Chem. Phys.*, **14**, 131 (1946).

[2] P. E. Yankwich, *ibid.*, **15**, 374 (1947).

[3] The solid occupied about half the volume of the sample tube. A stream of dry helium was passed through the crystals before the tube was sealed.

[4] A test carried out on an ammonium chloride sample irradiated and handled in similar fashion indicated no appreciable radioactivity in the gas phase above the sample after irradiation.

[5] The carrier solutions were all 1 *M* in the particular compound and 0.01 to 0.1 *M* in hydrochloric acid. Five ml. of each carrier solution was used. Because of its great reactivity formaldehyde was mixed with methanol and formic acid in one funnel, cyanide and methylamine being combined in another.

[6] Obtained from Mine Safety Appliances Co., Pittsburgh 8, Pa.

[7] When methyl bromide was included as a carrier it was found to be partially oxidized to carbon dioxide by Hopcalite at the sweep flow rate employed.

[8] Here only, TNG does not include cyanide radioactivity.

[9] Later experimentation showed that if the initial *p*H were about 9.7, both tarring and disproportionation of formaldehyde were prevented during the distillation, and quantitative recoveries could be achieved.

distillation contained the formaldehyde carrier in the form of sodium formate, while the distillate contained the methanol fraction.

One must start analyses of this kind with a guessed-at list of carriers, hoping to discover others suitable for activities found actually to be present as the study proceeds. At the end, ten or more carriers may be required; it is apparent that their quantitative separation, free from contamination, in a single experiment represents a noteworthy feat. It was decided, instead, to isolate only two or three carriers per run; while this attack leaves something to be desired, more strict control can be maintained over conditions of derivative formation, etc., than would otherwise be the case. The procedures employed in these fishing runs are given below. In runs of this type, the solution of target was prepared and gaseous activities removed as described above, except as noted below. The separations of non-gaseous carriers were performed on one aliquot of the degassed solution, TNG being determined with another. From time to time the total activity per gram of target, or the relative proportions of gaseous (TG) and non-gaseous (TNG) activities were determined.

Fishing Procedures

Carbon Dioxide.—Direct absorption as described above.

Carbon Monoxide.—Differential combustion as described above, except that methyl bromide carrier was removed by interposing before the Hopcalite-filled U-tube a trap cooled in liquid nitrogen or a reactor containing alkaline thiosulfate solution at 90–95°.[10]

Methyl Bromide.—The cold trap was evacuated momentarily to remove traces of methane and carbon monoxide. As the trap was warmed to room temperature its contents were swept through the copper oxide-filled furnace tube.

Methane.—Differential combustion with methyl bromide removal as described above.

Hydrogen Cyanide.—Silver cyanide–halide precipitation.

Methylamine.—An aliquot of degassed target solution was brought to *p*H 9 with dilute base and extracted with four 30-ml. portions of chloroform[11]; the combined organic layers were dried by shaking for two hours with anhydrous sodium sulfate, then treated with dry hydrogen chloride gas. The precipitated methylamine hydrochloride was removed by filtration, washed with a small amount of dry chloroform and dried for 10–15 minutes at 110°; a weighed portion was converted to carbonate by boiling alkaline permanganate.

Formic Acid.—An aliquot of degassed target solution was neutralized with dilute base. Five ml. of 1 *M* acetic acid and 30 ml. of a solution made by dissolving 100 g. of mercuric acetate in 1 liter of 0.5 *M* acetic acid were added. The mixture was brought to a boil and the carbon dioxide evolved swept into a sodium hydroxide-filled absorber.[12]

Formaldehyde.—To a neutralized aliquot of degassed solution of ammonium bromide target was added 6 ml. of a saturated ethanol solution of Methone (dimedon). After 8–12 hours standing, the precipitate was removed by filtration, washed with cold 50% aqueous ethanol, recrystallized from hot water–ethanol mixtures, and dried at 110° for 20–40 minutes.[13] A weighed portion was converted to carbon dioxide over copper oxide at 700–750° for use in the radioactivity determination.

Methanol.—Cyanide and methylamine were removed from an aliquot of degassed target solution by the precipitation and distillation methods discussed above. Formaldehyde was oxidized to formate by peroxide and the methanol fraction removed by distillation.

Urea.—An aliquot of degassed solution of the ammonium halide target material was brought to *p*H 6.5–7.0 with a phosphate buffer system and 100 mg. of jack bean urease added. After 15–20 minutes 10 ml. of 6 *N* sulfuric acid was added and the carbon dioxide evolved swept into sodium hydroxide solution.

Guanidine.—A boiling solution of 350 mg. of picric acid in 30 ml. of water was added to an aliquot of degassed target solution. When the mixture had cooled, guanidine picrate was removed by filtration, washed with cold water, recrystallized from hot, then dried for 1 hour at 110°. A weighed portion was converted to carbonate by treatment with boiling alkaline permanganate.

Methylhydrazine.—An aliquot of acidified target solution was evaporated to low volume, adjusted to *p*H 6 with dilute base and 0.15–0.20 ml. of liquid benzaldehyde added. After 30 minutes the mixture was brought to *p*H 1 with dilute sulfuric acid, then cooled in an ice-bath for 12 hours. The hydrazone was removed by filtration, washed with ice-water, and burned to carbon dioxide in a copper oxide-filled furnace tube.

Radioactivity Determinations.—Each carrier isolate was converted by oxidation to carbonate or carbon dioxide, thence to barium carbonate. For radioactivity determination a weighed aliquot of such barium carbonate was treated with concentrated sulfuric acid on a high vacuum system, and the carbon dioxide evolved transferred to an ionization chamber. The total pressure in the chamber was adjusted to 76 cm. with inert carbon dioxide. The ion current due to the disintegration of C^{14} in the chamber was determined with a vibrating-reed electrometer. Since the activity of the irradiated ammonium bromide was of the order of 3×10^4 dis. sec.$^{-1}$ g.$^{-1}$, the error in the radioactivity determinations, except for the least active fractions, could be reduced easily to a level of significance far less than that of errors inherent in the chemical fractionation and purification procedures.

Where possible, the percentage activity values given below were based on total radioactivity recovered. In cases where derivatives were prepared, or where isolating reactions were found to be partially complete, the final data were computed necessarily from specific activity information. Except where recovery was so low that blank corrections were appreciable compared with the amount of carbonate obtained, or where dilution corrections were very large (as with the Methone derivative combustion), the two calculations yielded essentially similar results.

Results of Chemical Fractionations.—The distribution of carbon radioactivity observed in the two preliminary experiments is given in Table I. All of the percentages are based on total recovery of radioactivity with the exception of those for cyanide, which are calculated from specific activity data. Because of the situations to which reference is made in the notes to Table I, only the carbon dioxide, cyanide and methanol fractions can be considered uncontaminated.

TABLE I

RADIOCARBON DISTRIBUTION: PRELIMINARY EXPERIMENTS

Fraction	Total activity, %	
CO_2	0.8	1.3
CO[a]	3.3	0.4
CH_4	6.7	7.7
HCN	2.9	2.1
Basic	78.4	77.4
HCOOH	4.1	2.7
HCHO[b]	6.1	7.8
CH_3OH	0.4	0.6
TNG[8]	86.3	88.5
Total	102.7	100.0

[a] No CH_3Br carrier present, so activity due to it may be in CO and CH_4 fractions. [b] Some tarring of HCHO observed.

In Table II are collected the percentage activity values based primarily on fishing experiments. The sum of all but the last is 101.3. In part, this sum reflects the errors due to blank and dilution corrections; however, its deviation from 100.0 is due also to the fact that not only was the total activity of the sample somewhat variable, but the distribution between gaseous and non-gaseous activities was not constant. These effects are shown in Table III, in connection with which it must be noted that the errors in radioactivity determinations for those samples are smaller than 0.5%; aliquoting and other errors may amount to 0.5–1.0%. There is a rough dependence of the change in distribution between TG and TNG and the date of analysis, indicative, perhaps of an effect of air with which the target material was in contact.

---

[10] C. G. Swain and C. B. Scott, THIS JOURNAL, **75**, 141 (1953).

[11] Polyfunctional bases and compounds such as methylhydroxylamine are not extracted.

[12] J. D. Reid and H. D. Weihe, *Ind. Eng. Chem., Anal. Ed.*, **10**, 271 (1938).

[13] W. Weinberg, *ibid.*, **3**, 365 (1931).

TABLE II

RADIOCARBON DISTRIBUTION: SUMMARY

Fraction	Total activity, %	
	Average	Values obtd.
CO_2[a,b]	1.7 ± 0.4	(0.8, 1.3), 1.5, 1.3, 2.1, 2.6, 1.9, 1.8
CO	1.3 ± 0.3	1.3, 1.3, 1.4
CH_3Br	1.8	1.8
CH_4	7.5	7.6, 7.4
HCN	2.0 ± 0.7	(2.9, 2.1), 2.5, 0.5
CH_3NH_2[c]	79.1 ± 1.3	78.2, 78.0, 81.0, [(78.7, 77.4), 77.0, 82.9, 79.4]
HCOOH	1.3 ± 0.5	2.6, 0.4, 0.6, 1.3, 1.2, 1.8, 1.5, 1.2
HCHO	5.8 ± 0.5	6.2, 5.1, 6.1
CH_3OH	0.4 ± 0.1	(0.4, 0.6), 0.3
$CO(NH_2)_2$	.4	0.4, 0.4
$CNH(NH_2)_2$	.0	0.0_0, 0.0_0
CH_3NHNH_2	<.9	0.0, 0.9[d]

[a] Appended error is average deviation from mean where three or more values obtained. [b] Values in parentheses from preliminary experiments. [c] First three values from fishing; values in brackets are total basic fraction. [d] Derivative was not recrystallized.

TABLE III

VARIATION OF ACTIVITY DISTRIBUTION[a]

Disintegrations/sec./g. of ammonium bromide	
TG	TNG
2,660	29,860
3,750	27,440
3,200	28,400
3,620	27,200

[a] Analyses performed at two-week intervals.

Discussion

Variation of Activity Distribution.—The variation in the distribution of carbon radioactivity between gaseous and non-gaseous carrier compounds is reflected in some of the results collected in Table II. Part of the scatter of percentages shown there is due certainly to analytical errors. The data for carbon dioxide, however, as well as that in Table III, seem to require that there operate other mechanisms than this for production of variations in the activity distribution. For example, a product precursor trapped in the ammonium bromide matrix might be capable of several different reactions with the solvent whose relative rates were very sensitive to *p*H, concentrations of traces of dissolved gases, etc., factors over which stringent control was not exercised.[14]

Origins of the Various Activities.—For purpose of discussion we shall assume that the radioactive bodies isolated with the various carriers are identical chemically to the carrier materials. The only obvious possible misapplication of this assumption would be to the total basic fraction which may contain very small amounts of some compounds for which analysis was not attempted, and even there the error would be small (see note *c*, Table II).

All C–Br and C–N linkages likely exist in the crystal before solution; thus the skeletons at least of methyl bromide, methylamine, cyanide and urea are formed as a consequence of the interaction of an energetic carbon with the ammonium and bromide ions. It seems likely that most of the C–H linkages also are formed in the crystal; not only are C–H bonds relatively strong and H abundant, but H would present a relatively small collision cross section to other atoms and would not, therefore, be easily *brushed off* a C whose energy had fallen to a level sufficiently low that combination with another atom was possible.

Since the ammonium halide crystals employed in this study were not subjected to *in vacuo* sublimation before irradiation, it is possible that carbon dioxide, carbon monoxide, formate, formaldehyde and methanol are produced by terminal interaction of some carbon-containing species with occluded air. On the other hand, cryosis of disturbed crystal near the end of the path of the recoil carbon might stabilize in the solid matrix species which would otherwise be highly reactive. These species are presumed to undergo reaction with solvent molecules at the moment of dissolution of the crystals. For example, a bromoimine such as HC(NH)Br could hydrolyze to yield either carbon monoxide or formic acid, while an imine such as $CH_2{=}NH$ could yield formaldehyde or, by reduction of water, carbon dioxide. Information as to the occurrence of these species and their reactions could be obtained from experiments in which non-aqueous solvents were employed.

The high yield of methylamine and the modest amount of methane formed are in accord with the argument above concerning stability of C–H linkages. The low yield of cyanide must be related to the difficulty of stripping an ammonium ion of its hydrogen, while the small amount of methyl bromide produced may be evidence for a generally negative charge on the carbon as it is thermalized. Formaldehyde would be expected to be more abundant than either methyl halide or formate on the basis of the above models, because an imine such as $CH_2{=}NH$ could be more easily formed than species containing covalent C–Br. Methanol might originate from a conglomerate such as CH_2, stabilized in the solid matrix in some fashion.

Acknowledgment.—We wish to express our thanks to Dr. W. R. Cornman, Jr., who assisted in the development and testing of some of the analytical procedures. This research was sponsored by the A. E. C.

URBANA, ILLINOIS

---

[14] Tests carried out on irradiated ammonium chloride gave no indication that the activity distribution depended upon whether or not any carriers were present in the solvent at the moment the sample was dissolved. Compare: W. S. Koski, THIS JOURNAL, **71**, 4042 (1949), where such dependence was found in the KCl (n,p)S^{35} system.