SYNTHESES WITH STABLE ISOTOPES: SODIUM CYANIDE-^{13}C, METHANE-^{13}C, METHANE-^{13}C-d_4, AND METHANE-d_4

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SUMMARY

Hydrogenation of carbon-^{13}C dioxide over ruthenium-on-alumina catalyst at 300-400°C produced methane-^{13}C, which was passed with excess ammonia over platinum at 1000°C to give, after absorption of the product in sodium hydroxide solution, sodium cyanide-^{13}C in 90% overall yield. Methane-^{13}C-d_4 and methane-d_4 were prepared by reduction of carbon-^{13}C monoxide and carbon monoxide, respectively, with deuterium.

Key Words: Carbon-^{13}C dioxide, carbon-^{13}C monoxide, methanol-^{13}C

INTRODUCTION

Cyanide is a basic starting material in many organic syntheses for introduction of an isotopic label. Most of the schemes developed for preparation of carbon-14 cyanide (1) can often be carried out conveniently on a scale of only a few millimoles, owing to the somewhat hazardous nature of the reactants and reaction when applied on a large scale. However, the reaction of barium carbonate-^{13}C with ammonium chloride and potassium has recently been applied to a preparation of potassium cyanide-^{13}C in approximately 50-millimole quantities (2). Reduction of carbon-^{13}C dioxide to elemental carbon-^{13}C followed by reaction with ammonia at 1100°C has produced cyanide-^{13}C in high yield (3). Dehydration of formamide-^{13}C, using triphenylphosphine-carbon tetra-

0362-4803/80/0217-0255$01.00
Received January 2, 1979
Revised March 28, 1979

chloride, to give sodium cyanide-^{13}C was found applicable to scales ranging from a few millimoles to a mole (4).

We wish to report the synthesis of methane-^{13}C, based on a method used in radiocarbon dating for reduction of carbon dioxide to methane (5). Conversion to cyanide-^{13}C by reaction of the methane with ammonia over platinum at 1000°C utilizes a reaction known for many years (6) and that has been applied to the carbon-14 (7) and carbon-11 (8) analogs. The methods described here were developed for relatively large-scale production and were subsequently found applicable to methane-d_4 and methane-^{13}C-d_4 as well as to smaller quantities of methane-^{13}C and cyanide-^{13}C. The mass-20 and -21 methanes are useful large-scale, nonradioactive, atmospheric tracers (9).

DISCUSSION

The reaction sequence for preparation of sodium cyanide consisted of catalytic hydrogenation of carbon dioxide to methane. Reaction of the methane with ammonia over hot platinum produced ammonium cyanide, which was converted to the sodium salt by sodium hydroxide.

$$CO_2 + 4H_2 \xrightarrow[300\text{-}400^\circ C]{Ru/Al_2O_3} 2H_2O + CH_4$$

$$CH_4 + 2NH_3 \xrightarrow[1000^\circ C]{Pt} NH_4CN + 3H_2$$

$$NH_4CN + NaOH \longrightarrow NaCN + NH_3 + H_2O$$

Carbon monoxide was also reduced and required only 3 moles of hydrogen.

The methanes were prepared in an apparatus that relied on convective circulation of the gases through the hot catalyst. A converter having a volume of 7 liters, similar to that developed for radiocarbon dating (5), allowed preparations up to 3 moles at a pressure of about 150 psig. A smaller unit, shown in Fig. 1, was constructed from a 1-liter stainless-steel cylinder.* During the

*This converter can be also used for the synthesis of methanol-^{13}C by using a different catalyst as previously described (10) contained in copper screen; the heating element was encased in quartz or copper to prevent formation of methane and carbon (11).

hydrogenation the vessel was immersed to about three-fourths its height in cooling water to promote convection and to condense the water produced.

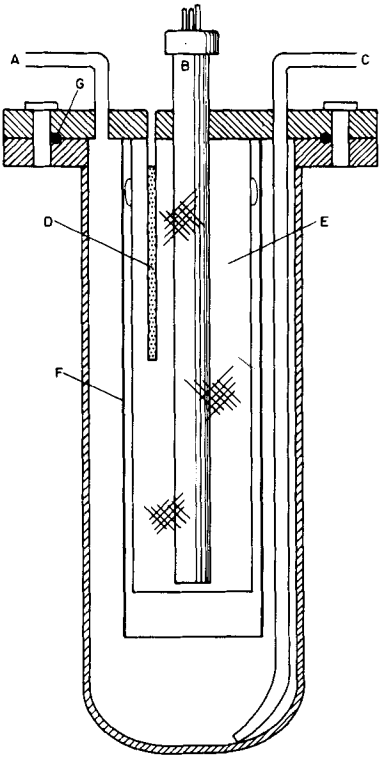

Fig. 1. Methane synthesis apparatus. A, gas inlet, B, 250-watt electric heater; C, liquid withdrawal tube; D, thermocouple well; E, catalyst (1/8-in pellets, 0.5% ruthenium on alumina) contained in stainless-steel screen; F, chimney; G, O-ring.

The reaction was carried out by pressurizing the apparatus with the desired quantity of carbon dioxide or monoxide, bringing the catalyst to about 300°C, and adding hydrogen or deuterium in increments from a cylinder of known volume and pressure.* The hydrogen

*Pressure is not required for the reaction, except as it affects scale; a continuous-flow apparatus for production of large quantities of isotopic methanes has been developed (12). A flow system was used for preparation of cyanide-^{14}C, by way of methane-^{14}C, from barium carbonate-^{14}C on a millimolar scale (7).

was added in amounts sufficient to produce a temperature rise to 350-400°C (too fast a rate could produce local overheating with damage to the heating element). After the temperature had returned to about 300°C, the process was repeated until reduction was complete as evidenced by no further evolution of heat and by the quantity of hydrogen used. The final pressure was essentially the same as initial pressure plus that from excess hydrogen. The water and methane were frozen into the bottom of the vessel with liquid nitrogen, the hydrogen was pumped off, and the methane was transferred and purified by distillation. The product, in yield of 94-98%, was quite pure as shown by infrared spectroscopy and gas chromatography. Traces of hydrogen or deuterium were occasionally detected, which could be removed, if necessary, by a palladium alloy diffusion cell (5). Very small amounts of carbon dioxide were also detected in a few runs and were readily removed by allowing the gas to remain over Lithasorb for several hours. Infrared absorption and gas chromatographic data are presented in Tables I and II.

Table I. Infrared absorption of methane isotope isomers.

Frequency (cm^{-1})[a]			
CH_4	$^{13}CH_4$	CD_4	$^{13}CD_4$
3040	3040	2260	2250
1300	1300	990	980

[a]To nearest 5 cm^{-1}.

Table II. Gas chromatographic separation of gases.

	Retention Time (min)[a]					
°C	CH_4, $^{13}CH_4$	CD_4, $^{13}CD_4$	H_2, D_2	CO	CO_2	N_2
5	47.6	43.8				6.7
25	11.4	10.6	0.5	3.3		2.2
100	3.9		0.7	1.7	8.7	1.5

[a]Carbosieve column, 1/8 in x 9 ft; helium carrier, 100 $cm^3 \cdot min^{-1}$.

Sodium cyanide-^{13}C was synthesized by passing methane-^{13}C and ammonia over platinum contained in a quartz combustion tube heated in a tube furnace to approximately 1000°C. The exit gases were passed, after preliminary cooling by a condenser, through a cold trap followed by a sodium hydroxide trap. The maximum flow rate for the methane was determined by infrared analysis (for absence of methane) of the gases emerging from the traps. Excess ammonia was needed to avoid formation of red-brown polymeric materials, which condensed at the outlet of the reaction tube. Even so a carbon mirror developed within the tube, but appeared to remain constant through many preparations.

Most of the product was condensed as ammonium cyanide-^{13}C in the cold trap and was combined with the remainder retained in the sodium hydroxide trap. Following analysis for total cyanide and addition of sodium hydroxide sufficient for equivalence, the aqueous solution of sodium cyanide-^{13}C was evaporated to dryness at reduced temperature and pressure. Recovery was almost quantitative and gave a product of approximately 96% purity (the remainder was presumably sodium hydroxide and water). The water-evaporation step was somewhat tedious, and could be avoided in future preparations by trapping the product in cold methanol, analyzing for the total amount of cyanide, adding the equivalent quantity of sodium (or potassium) hydroxide, and isolating by vacuum evaporation of the alcohol (13).

Dependence of the reaction on the amount and form of the platinum catalyst was not investigated extensively. Most reactions were conducted on a relatively large scale; however, a smaller unit was developed which performed satisfactorily with less than 10 g of platinum. Platinized asbestos was investigated briefly and found difficult to pack in the 1-cm tube, and to give low yields (20-35%), even at low flow rates, in the 2.5-cm tube (25 g, 5% platinum).

EXPERIMENTAL

Materials and Methods--Carbon-^{13}C dioxide and carbon-^{13}C monoxide at approximately 90 atom % ^{13}C were produced by the Los Alamos Scientific Laboratory Stable Isotope Separation Facility (14). The ruthenium catalyst (0.5% on alumina) was from Strem Chemicals, Inc. Infrared spectra were determined in the gas phase on a Perkin-Elmer Model 710 and are reported to the nearest 5 cm^{-1} (Table I). A Varian Model EP90 was used for gas chromatography (Table II). Cyanide analysis was by titration with silver nitrate using potassium iodide as indicator.

Methane-^{13}C--Carbon-^{13}C dioxide (94.3 g, 2.10 mol, 95 psig) was introduced into the evacuated 7-L converter (5) and the catalyst bed was heated to about 300°C (the pressure was then approximately 130 psig). With the lower portion of the converter in cooling water or ice, hydrogen was added from a calibrated 8-L cylinder (45 psi/mol) in increments of 20 to 50 psi, which caused a temperature rise of the catalyst bed to 350-400°C; subsequent additions were made after the catalyst bed returned to 300°C. After addition of 8.5 mol of hydrogen (380 psi decrease in the hydrogen cylinder pressure) during about 5 hr, temperature rise no longer occurred, and the converter pressure remained constant. The bottom of the reactor was cooled, first with Dry Ice and then with liquid nitrogen, and the excess hydrogen was pumped out through a charcoal-filled trap cooled by liquid nitrogen.* The liquid-nitrogen baths were removed from the base of the converter and from the charcoal trap, and the product was transferred into a liquid-nitrogen cooled 1-L gas cylinder (34.1 g, 725 psig, 96% yield).** The infrared spectrum (5-cm gas cell, 0.5-atm pressure) showed no carbon monoxide or dioxide. Gas

*The vapor pressure of methane at liquid nitrogen temperature is quite high (approximately 10 mm Hg); therefore, pumping should not be prolonged or the capacity of the charcoal may be exceeded.
**Residual methane remaining in the apparatus amounts to only a fraction of a percent.

chromatography indicated a very small amount of hydrogen. Proton NMR (CCl_4): δ 0.22, J_{CH} 126 Hz.

The other isotope isomers were similarly prepared using either the above apparatus or the 1-L converter shown in Fig. 1 and with either carbon dioxide or monoxide. Water from the previous run was removed through the withdrawal tube (or, in the large converter, through a valve in the base) followed by evacuation. In changing from one hydrogen isotope to the other, a small-scale (approximately 0.1-mol) purging reaction using normal-abundance carbon dioxide or monoxide was carried out to remove residual gas absorbed on the catalyst.

Sodium Cyanide-^{13}C--Methane-^{13}C (19.5 g, 1.15 mol) at 0.17 L/min and excess ammonia at 0.55 L/min were passed through a quartz reaction tube (2.5 by 90 cm) containing a rolled platinum perforated sheet (138 g, 31-cm length) and platinum gauze (138 g, 12-cm length) that was heated by an electric tube furnace to 1000°C. The exit gases were passed through an air-cooled spiral condenser into an ice/alcohol-cooled trap at -20°C and then through sodium hydroxide solution (5 M, 200 mL). The contents of the sodium hydroxide trap (containing 0.53 mol of cyanide-^{13}C) were combined with the ammonium cyanide (24.8 g, 0.55 mol) in the cold trap (which was kept cold at all times), and additional sodium hydroxide (0.08 mol) was added. The solution was evaporated at reduced pressure and temperature to give 55.5 g of white powder (1.07 mol by argentimetric titration, 93% yield).

Sodium Cyanide-^{13}C (Small-Scale Synthesis)--Methane (3.2 g, 0.20 mol) at 0.07-0.09 L/min and ammonia at 0.43-0.45 L/min were passed during about 2 hr through a quartz reaction tube (1.2 by 90 cm) containing 4 sheets of rolled and crumpled platinum foil (7.8 g) distributed along 80 cm of the tube and heated to approximately 1000°C. The product was trapped as in the above preparation to give ammonium cyanide (7.5 g, 0.17 mol) and sodium cyanide (0.01 mol) (90% yield).

ACKNOWLEDGMENT

This work was performed under the auspices of the U. S. Department of Energy.

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