RAPID SYNTHESIS OF ISOTOPICALLY LABELLED METHANES*

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SUMMARY

The reaction between carbon monoxide and hydrogen to form water and methane proceeds quantitatively in a single pass through a supported Ni catalyst bed at 250 - 350°C in an atmospheric-pressure flow system. The system described is capable of rapid, continuous production of isotopically labelled methanes.

Key Words: Carbon-^{13}C Monoxide, Deuteromethane-^{13}C, Flow System, Methane Synthesis.

INTRODUCTION

The synthesis of methane-^{13}C in a batch process has been described earlier (1). More recently, in connection with atmospheric tracer experiments using isotopically labelled methanes, the need arose for a synthetic process capable of producing such materials at a much more rapid rate using carbon monoxide and hydrogen as reactants. This lead to development of an atmospheric-pressure, Pyrex-glass flow system (shown schematically in Figure 1) in which the reaction

$$CO + 3\ H_2 \rightarrow CH_4 + H_2O$$

produces 1 mol per hour of the desired methane when a mixture of ∿3.5 H_2 per CO (to ensure XS H_2 which also serves as a sweep gas) is passed over a suitable catalyst at 250 - 350°C. The system has been used to prepare

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$^{13}CD_4$, $^{13}CH_4$, $^{12}CH_4$, $^{12}CD_4$ and mixtures of $^{13}CH_xD_{4-x}$ by using the appropriately labelled carbon monoxide in conjunction with either D_2, H_2, or H_2-D_2 mixtures. The yield of methane is quantitative within the uncertainty of measurement of total CO processed (±2%). Mass-spectrometric analysis of the methane produced shows small amounts of unreacted CO (of the order of 0.2%) as the only detectable impurity. In the system shown in Fig. 1, the total amount of methane which can be produced in a continuous run is limited by the capacities of the traps which condense the water and methane. (In the present system, the methane trap can hold up to 6 moles of methane.) However, if desired, the process could be made completely continuous by providing a second trapping system, identical to the one shown, into which the product stream could be diverted while the products in the first system were being recovered.

The trapping system shown in Fig. 1 catches the bulk of the water in receiver TR1 cooled in an ice-H_2O bath. The ensuing dry-ice trap TR2 removes residual water from the methane and excess hydrogen. Similarly, trap TR3, cooled in liquid N_2, catches the bulk of the methane while trap TR4, also cooled in liquid N_2, catches ~2% or less of the total methane recovered. Since methane at liquid N_2 temperature is a solid with equilibrium vapor pressure of ~10 torr (2), some product is carried away in the exit stream of excess hydrogen. Under the experimental conditions described, loss of methane by this route is less than 1% of the total methane produced and has, therefore, been ignored. (This material can be caught on Linde 5A molecular sieves at liquid N_2 temperature (3) but separation of the methane from the concurrently absorbed hydrogen is tedious.)

Two catalyst preparations have been tested and both found capable of producing methane from carbon monoxide and hydrogen in essentially quantitative yield at the rate of 1 mole per hour in the flow system described. One is a commercial preparation of 0.5% Ru on 1/8" x 1/8" γ-Al_2O_3 pellets (4)

and the other a "homemade" preparation of ~5% Ni on the same support. In each case, a catalyst bed 55 mm in diameter by 6 cm long (containing ~150 g of catalyst) operating at an indicated temperature of 250 - 350°C (read on a Cr-Al thermocouple near the center of the catalyst bed, cf. Fig. 1), served the required purpose. Dissipation of the heat of reaction is an important consideration since it is exothermic to the extent of ~50 Kcal per mole (5). Thus, at a production rate of 1 mole per hr, the reaction itself is putting ~60 watts of heating into the reaction zone. Unless this heat is effectively dissipated, the indicated temperature may, even in the absence of added heat from the furnace, exceed 400°C whereupon there is a measurable decrease in yield of methane and a noticeable deposit of carbon in the reaction zone. It is, therefore, desirable to facilitate heat transfer out of the reaction zone by using a minimally insulated furnace regulated to maintain the catalyst bed at 250°C in the absence of reaction. With the reaction proceeding at 1 mole per hour of methane, the indicated temperature in the system described typically increases to a steady-state value of 300 - 350°C with the furnace in place but with its power turned off.

EXPERIMENTAL

Carbon-^{13}C monoxide at 90 - 93 atom % ^{13}C was produced by the Los Alamos Stable Isotope Resource (6).

The "homemade" Ni catalyst now used routinely in this synthesis may be prepared as follows:

Dissolve 75 g $Ni(NO_3)_2 \cdot 6H_2O$ (Baker Analyzed Reagent, F. Wt. = 291) in distilled H_2O to a final volume of 150 mℓ. In a 1000 mℓ Erlenmeyer flask, wash 300 g of 1/8" x 1/8" γ-Al_2O_3 pellets (Strem Chemicals, Inc., Danvers, Mass.) with distilled H_2O by decantation to remove fines. Add the 150 mℓ of $Ni(NO_3)_2$ solution to the moist Al_2O_3 pellets in the 1000 mℓ Erlenmeyer flask and pump off H_2O using a "Roto-Vap" apparatus with aspirator pumping and the Erlenmeyer flask rotating while partially submerged in a 40°C bath.

When all the liquid is gone, transfer the particles to a 1 liter beaker and dry overnight in a 100°C oven. The preparation now consists of light green pellets of Al_2O_3 impregnated with $Ni(NO_3)_2$. Convert the $Ni(NO_3)_2$ to NiO by heating the pellets in air (∿75 g at a time in a 17.5 cm evaporating dish over a Meker burner) with stirring until evolution of brown oxides of nitrogen is no longer observed. The particles should now consist of a uniform, medium-grey dispersion of NiO on Al_2O_3. Before use, reduce the NiO to Ni by heating the pellets to ∿350°C in a stream of H_2 for 24 - 48 hr. The final catalyst is uniform dark grey.

A typical run proceeds as follows: With a slow flow of hydrogen (∿5 STPL/hr) through the system, turn the thermoregulated furnace on and wait until the indicated temperature in the catalyst bed is regulating at 250°C. With all traps immersed in appropriate cooling baths, increase the hydrogen flow to 78 STPL/hr and introduce the carbon monoxide at 22 STPL/hr into the hydrogen stream. Within a few minutes, the following observations should be made: 1) a decrease in flow of gas at the system exit (from ∿100 STPL/hr to ∿12 STPL/hr); 2) noticeable condensation of water and methane in their respective traps; and 3) a significant rise in indicated temperature of the catalyst bed. Within an hour or so the indicated temperature in the catalyst bed should have reached a steady state, not to exceed 400°C. Except for occasional replenishment of coolant in the various cold baths, the system runs continuously with little attention until the water and methane collectors require emptying; in the system described here, a maximum of 6 hr. At this point, the carbon monoxide flow is shut off, then the hydrogen flow reduced to 10 - 20 STPL/hr and allowed to continue for ∿15 minutes more to ensure that all water and methane have been swept out of the reaction zone into their respective traps. The methane traps are then isolated from the flow system and pumped on at liquid-N_2 temperature to remove hydrogen. The liquid-N_2 baths are then removed and the methane transferred through the

vacuum manifold into a previously evacuated and liquid-N_2-cooled stainless steel cylinder equipped with a high-pressure metal valve.

Typical mass-spectrometric analysis of methane prepared from ordinary carbon monoxide (98.9% ^{12}CO, 1.1% ^{13}CO) and high purity D_2 (>99.5%) is: 98.8% $^{12}CD_4$, 1.0% $^{13}CD_4$, 0.2% $^{12}C^{16}O$.

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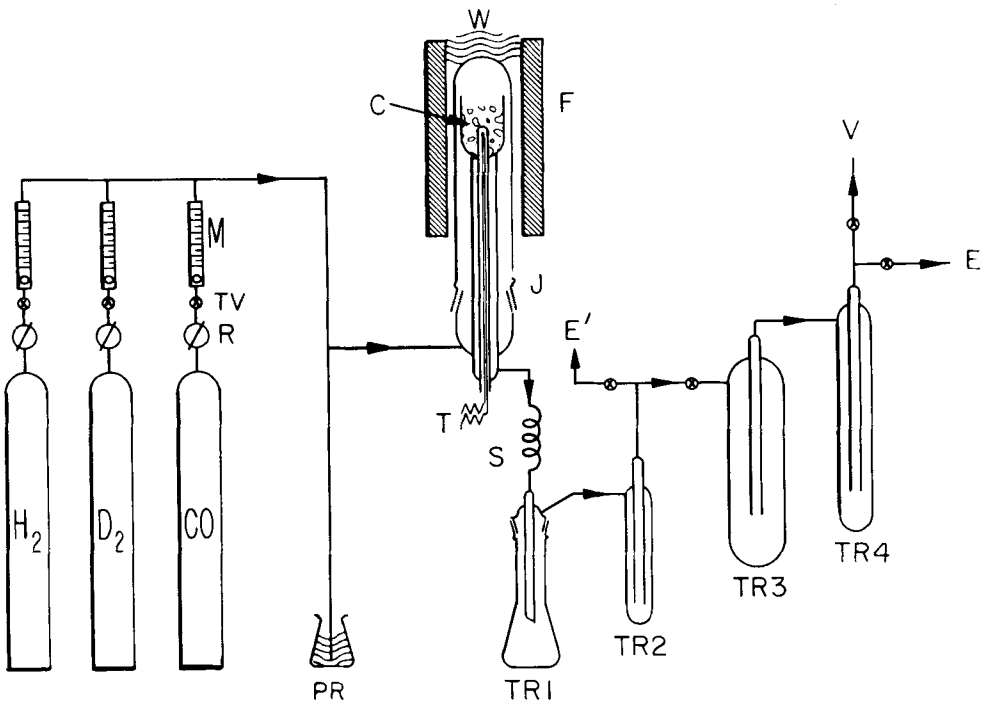

Figure 1

Atmospheric-Pressure Flow System: R, pressure regulators; TV, throttling valves; M, flowmeters; PR, mercury pressure-relief; C, catalyst bed; W, Pyrex-wool insulation; F, thermoregulated furnace; J, 71/60 standard-taper Pyrex joint; T, thermocouple; S, 8 mm o.d. standard-wall Pyrex, air-cooled spiral; TR1-4, traps described in text; E, exit to atmosphere; E', alternate exit to atmosphere; V, connection to vacuum manifold. All connecting tubing is 8 mm o.d. standard-wall Pyrex and, unless otherwise specified, valves are Kontes, Pyrex and Teflon valves with viton O-ring seats.