

CARBON ISOTOPIC COMPOSITIONS OF INDIVIDUAL HYDROCARBONS, CARBON DIOXIDE, AND OILS FROM THE FISCHER-TROPSCH REACTION; K. Wedeking, R. Shipp, and S. Chang, Extraterrestrial Research Division, NASA-Ames Research Center, Moffett Field, CA 94035; E. Rightor and T.J. Pinnavaia, Department of Chemistry, Michigan State University, East Lansing MI 48824.

Fischer-Tropsch type reactions operating in the solar nebula have been proposed to account for the organic matter and the CO<sub>2</sub> bound as carbonate in carbonaceous meteorites (1,2). Previous work on the carbon isotopic fractionation in the Fischer-Tropsch reaction has been limited to the work of Lancet (1) and Lancet and Anders (2). These workers have reported closed system isotopic fractionations associated with the formation of CO<sub>2</sub>, methane, a fraction containing C<sub>2</sub> and greater chain length hydrocarbons, and wax from reactions run at 127°C and 227°C. To date, no information is available regarding the isotopic compositions of individual hydrocarbons produced in the Fischer-Tropsch reaction, which could provide an identifiable "signature" for comparison with hydrocarbons in meteoritic materials of cosmochemical significance (3). To identify such a signature is the major thrust of this report.

Reactions were carried out using iron catalysts in open flow systems at two different pressures. Reactions were run at 8.2 atmospheres and 275°C with an iron-montmorillonite catalyst; those at one atmosphere and 305°C with a 50:50 iron carbonate-kieselguhr catalyst. Isotopic compositions of individual hydrocarbons and CO<sub>2</sub> were determined by GC-combustion followed by mass spectrometric analysis of CO<sub>2</sub> samples. Oil samples were analyzed by sealed-quartz-tube CuO combustion.

Products formed in amounts sufficient for analysis by GC-combustion in the 8.2 atmosphere syntheses included C<sub>1</sub>-C<sub>5</sub> normal saturated hydrocarbons, propylene, and CO<sub>2</sub>. Concentrations of each product analyzed by GC-combustion were determined gas chromatographically. In one experiment the most abundant product was CO<sub>2</sub> at 639 umol per liter of product gas at room temperature and one atmosphere pressure (4.7% molecular yield). C<sub>1</sub>-C<sub>5</sub> normal saturated hydrocarbons dropped off sharply in concentration from methane at 556 umol/L (4.1% yield) to pentane at 12.8 umol/L (0.094% yield). Propylene was the only olefin present in significant abundance at 1.86 umol/L (0.014% yield).

Isotopic fractionations observed in the 8.2 atmosphere experiments were generally consistent with those reported by Lancet (1) for similar conditions. C<sub>2</sub>-C<sub>5</sub> normal saturated hydrocarbons were similar in isotopic composition, with fractionations relative to the source CO of -24 to -30%. Methane, however, was observed to be consistently heavier than C<sub>2</sub>-C<sub>5</sub> hydrocarbons by 7-20%. The minor component, propylene, was heavy relative to C<sub>2</sub>-C<sub>5</sub> hydrocarbons by 7%. CO<sub>2</sub> was depleted in <sup>13</sup>C relative to source CO by 9%.

Products in the one atmosphere syntheses (carried out in duplicate), though including saturated hydrocarbons, were dominated by olefins. Absolute quantities of these products

obtained in a 5 hour reaction averaged to the following values: ethane, 0.2  $\mu\text{mol}$  ( $1.6 \times 10^{-4}$  % yield); ethylene, 1.4  $\mu\text{mole}$  ( $1.1 \times 10^{-3}$  % yield); propylene, 1.4  $\mu\text{mol}$  ( $1.1 \times 10^{-3}$  % yield); butylene, 0.6  $\mu\text{mol}$  ( $4.9 \times 10^{-4}$  % yield).  $\text{CO}_2$ , though observed, was not analyzed isotopically in the one atmosphere syntheses, nor was methane. Propane and butane were also produced, but in yields lower than that of ethane.

Isotopic fractionations observed in the one atmosphere syntheses were also generally consistent with those reported by Lancet (1). As was seen in the high pressure experiments, the major products, ethylene, propylene, and butylene, were isotopically light relative to source CO by some 24%, with no systematic variation in isotopic composition with carbon number. The minor component, ethane, had an isotopic composition nearer that of the source CO. Three oil samples obtained by synthesis at one atmosphere were consistently light relative to source CO, with an average of -24%, similar to the compositions of the major olefinic products.

As a result of this work, a consistent picture is beginning to emerge regarding the probable isotopic signature of the Fischer-Tropsch reaction products at elevated temperatures. With the exception of methane, major hydrocarbon components, independent of carbon number or degree of saturation, are isotopically light by some -24 to -30% relative to source CO, while minor components are somewhat heavier than the major products, as are methane and  $\text{CO}_2$ . In future work we plan to extend these experiments to reactions run at temperatures as low as  $130^\circ\text{C}$ .

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REFERENCES: (1) Lancet, M. (1972) Ph.D. Dissertation, University of Chicago. (2) Lancet, M. and Anders, E. (1970) Science 170, 980-982. (3) Yuen, G., Blair, N., Des Marais, D., and Chang, S. Nature 307, 252-254.