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Carbon Isotope Fractionation in the Fischer-Tropsch Synthesis and in Meteorites

Abstract. *Carbon dioxide and organic compounds made by a Fischer-Tropsch reaction at 400°K show a kinetic isotope fractionation of 50 to 100 per mil, similar to that observed in carbonaceous chondrites. This result supports the view that organic compounds in meteorites were produced by catalytic reactions between carbon monoxide and hydrogen in the solar nebula.*

Most of the carbon in carbonaceous chondrites exists in reduced form, largely as an aromatic polymer and, to a lesser extent, as extractable organic compounds (*1*). A minor part (~ 3 to 5 percent) exists in oxidized form, as the carbonates breunnerite [$(Mg,Fe)CO_3$] and dolomite [$MgCa(CO_3)_2$] (*2*).

These two types of reduced carbon differ greatly in their isotopic composition. The polymeric carbon is light: $\delta C^{13} = -15$ to -17 per mil in both type I and type II carbonaceous chondrites (*3*). The carbonate carbon is much heavier: $\delta C^{13} = +60$ to $+70$ per mil in type I and $+40$ to $+50$ per mil in type II carbonaceous chondrites (*3*, *4*), for a total difference of 83 to 87 and 57 to 67 per mil. For comparison, terrestrial organic matter and carbonates (including that formed cogenetically, for example, by shellfish) generally differ by only about 25 per mil, typical values being -25 to -30 per mil for organic carbon and ~ 0 per mil for carbonates. The meteoritic carbonates fall well outside the range of terrestrial carbon, -80 to $+25$ per mil (*5*).

Clayton (*4*) has considered four possible origins of the meteoritic carbon isotope fractionation. The first of these possibilities, single-stage equilibrium fractionation, can, in principle, give an effect of the right sign and magnitude. Data for organic molecules of appropriate complexity are unavailable, but if calculations for CH_4 and CO_2 (*6*) are used as a first-order approximation, temperatures of 265° to 335°K would seem to be required for the observed fractionations in type I and type II carbonaceous chondrites. However, no mechanisms on earth are known that would establish equilibrium at the lower of these temperatures. Kinetic isotope effects are a second alternative, but in the reactions studied thus far, the fractionation was too small (20 to 40 per mil) and in the wrong direction, the oxidized carbon becoming lighter rather than heavier (*7*). The third possibility, biological activity, produces fractionations of the right sign, but usually of insufficient magnitude [algae, 10 to 12 per mil; vascular plants, 20 to 30 per mil (*8*)]. Finally, it is conceivable that the differences reflect nuclear processes, the two types of carbon having had different histories of nucleosynthesis. This alternative was favored by Urey (*9*). However, all work to date has failed to bring to light any isotopic differences that might be attributed to incomplete mixing in the solar nebula.

The origin of the organic compounds is, of course, pertinent to this problem. Studier *et al.* (*10*) have shown that nearly all compounds identified in meteorites can be produced by a Fischer-Tropsch type of reaction between CO, H_2, and NH_3 in the presence of a nickel-iron or magnetite catalyst. They proposed that the organic compounds in meteorites were made by such reactions, catalyzed by dust grains in the solar nebula.

The Fischer-Tropsch reaction produces both oxidized and reduced carbon. Much of the oxygen from CO usually is converted into H_2O (Eq. 1), but a variable proportion is converted to CO_2 (Eq. 2):

$$n\,CO + (2n+1)\,H_2 \rightarrow C_nH_{2n+2} + n\,H_2O \qquad (1)$$

$$2n\,CO + (n+1)\,H_2 \rightarrow C_nH_{2n+2} + n\,CO_2 \qquad (2)$$

Nothing is known about carbon isotope fractionation in this reaction, however. We, therefore, decide to investigate it.

A difficulty encountered in our experiments was the tendency of any CO_2 formed to disappear by secondary reactions. [Hydrogenation of CO_2 to hydrocarbons is thermodynamically feasible (*11*).] We circumvented this problem by collecting CO_2 as fast as it was formed, using a $Ba(OH)_2$ absorbent.

For our syntheses, we heated 0.8 liter of an equimolar mixture of CO and H_2, initially at 1 atm, to 400° ± 10°K in a Vycor flask in the presence of 1.5 g of cobalt catalyst (*12*). (Cobalt was chosen because it is effective at lower temperatures than iron catalysts; otherwise there is little difference between the two.) As the reaction progressed CO_2 was removed continuously by absorption in 5 ml of a saturated $Ba(OH)_2$ solution in a 35-ml sampling tube, connected to the reaction vessel by a side arm. The sampling tube was replaced from time to time. In order to ensure complete recovery of all CO_2 formed during the sampling interval, the tube was cooled to −196°C just before removal. All condensable gases were thus frozen out. After closing the stopcock between the sampling tube and the reaction flask, we warmed the tube to room temperature and shook it to promote absorption of CO_2. The stopcock was opened briefly to equalize pressure, and the sampling tube was replaced by a new one.

The gas phase was separated into three fractions: CO, CH_4, and heavier hydrocarbons (C_{2+}). Those components that remained gaseous at −196°C (CO, H_2, and CH_4) were passed over CuO at 150°C. This reaction converted CO to CO_2 and H_2 to H_2O, which were frozen out. The CH_4 remaining was oxidized to CO_2 by passage over CuO at 850°C. Trial runs showed that this procedure separated CO from CH_4 with 99.1 to 99.5 percent efficiency.

The fraction condensed at −196°C (the "C_{2+} fraction"), which consisted of hydrocarbons heavier than CH_4, was oxidized to CO_2 by passage over CuO at 850°C. Finally, the original CO_2 fraction was recovered from the $BaCO_3$-$Ba(OH)_2$ suspension by the addition of 85 percent H_3PO_4 to the sampling tube. The volume of each fraction was determined on a mercury manometer.

Because of the nature of our sampling procedure, the CO_2 fraction was not quite comparable to the other three fractions. It was removed continuously from the entire reaction volume, and thus represents the *incremental* yield between successive samplings. The other three fractions were isolated from small portions of the gas phase and thus represent *cumulative* yields. We cannot completely rule out the possibility that the CO_2 was slightly fractionated as a result of incomplete freezing out and absorption. This result would tend to make the recovered CO_2 too light. A control experiment showed, however, that CO_2 recovery was ≧ 89 percent complete in 4 hours, our shortest sampling interval. Moreover, the CO-CO_2 fractionation remained constant throughout the experiment as sampling times increased.

Isotopic compositions were measured on a 15-cm, 60°-sector double-collecting mass spectrometer (*13*). All results are given relative to the Pee Dee belemnite (PDB) standard. The isotopic measurement itself is usually accurate to ± 0.1 per mil. However, samples smaller than 40 μmole had to be diluted with standard CO_2 before measurement, and, since our initial procedure for measuring small gas volumes was not accurate enough, uncertainties in the dilution factor led to rather large errors in isotopic composition.

The results reported here are based on two experiments under nominally identical conditions, comprising a total of eight fractions (Table 1). The catalyst in experiment 2 seems to have been slightly less active, judging from the slower rate of reaction. In combining the results on a single graph, we have therefore used degree of conversion rather than time as the abscissa (Fig. 1).

Table 1. Carbon isotope fractionation in Fischer-Tropsch synthesis; equimolar ratio of CO to H_2; temperature = 400°K; pressure = 1 atm; cobalt catalyst.

Time (hr)	Percentage of total*				δC^{13} (‰)†			
	CO	CH_4	C_{2+}	CO_2	CO	CH_4	C_{2+}	CO_2
					Experiment 1			
7	90.2	8.2	0.5	0.05	−37.6	−81.2	−30 ± 30	0 ± 9
31	30.5	68.6	0	0.05	−46.8	−38.5		−8 ± 6
58	15.8	80.7	1.5	0.10	−47.7	−35.1	−61 ± 3	−11.5 ± 3
320	8.1	87.9	3.3	0.68	−48.0	−35.3	−62.2	−11.1
					Experiment 2			
4	95.6	1.9	1.5	0.05	−37.3	−100 ± 4	−62 ± 3	−1 ± 5
15	93.8	3.5	1.7	0.05	−37.4	−94 ± 3	−55 ± 2	
30	64.7	29.4	2.3	0.18	−33.1	−50.2	−61.2	−5.3
217	24.1	69.0	3.0	0.20	−47.2	−37.1	−63.1	−11.1

* Values for CO, CH_4, and C_{2+} were determined on a 1/20th aliquot and reflect the composition of the gas phase at the time of sampling. Carbon dioxide, on the other hand, was removed continuously from the entire reaction mixture. The amounts given in the table are 1/20th of the amount actually collected and refer to the CO_2 formed between consecutive sampling intervals. † Initial CO: −38.6 per mil. Errors are ± 0.1 per mil, unless otherwise indicated. A "wax" fraction was recovered from the catalyst in experiment 1 at the end of the reaction. It comprised 1.5 percent of the total carbon and had a δC^{13} of −72.2 per mil.

A strikingly large fractionation (~ 100 per mil) between CH_4 and CO_2 appears in the early stages of the reaction. The equilibrium fractionation at 400°K is only 45 per mil (*6*), and so this is clearly a kinetic isotope effect.

As the reaction progresses, the methane becomes isotopically heavier. This is due in part to material balance: as CH_4 becomes the dominant product, it must, of necessity, approach the isotopic composition of the starting material. This trend seems to be further enhanced by isotopic equilibrium. The CH_4-CO fractionation approaches the equilibrium value of 15 per mil (*14*) in the latter stages of the reaction. Apparently the CH_4-CO exchange is fairly rapid under our experimental conditions.

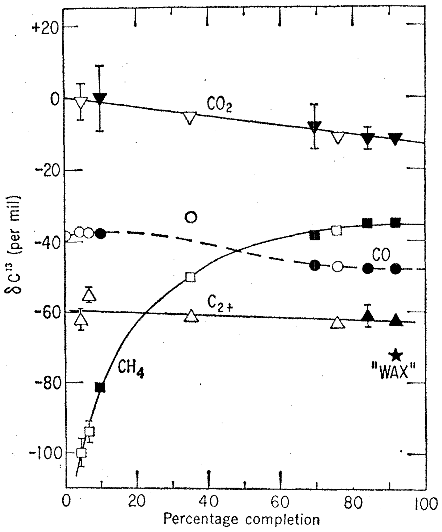

Fig. 1. Carbon isotope fractionation in the Fischer-Tropsch reaction at 400°K. Solid symbols, experiment 1; open symbols, experiment 2. In the early stages of the reaction CH_4 shows a fractionation as large as 100 per mil relative to CO_2. Hydrocarbons of higher molecular weight (C_{2+}, "wax") show smaller fractionations (50 to 60 per mil) which, however, persist throughout the reaction.

The C_{2+} fraction is perhaps more pertinent to the meteorite problem, because the bulk of the reduced carbon in meteorites consists of polymeric material and molecules with ten or more carbon atoms. This fraction remains ~ 50 per mil lighter than the CO_2 throughout the reaction, as its amount increases from ~ 0.5 to ~ 3 percent. Apparently, its rate of exchange with CO is much slower than that of CH_4.

Because of the nature of our experiment, the C_{2+} fraction was not truly representative of all heavy hydrocarbons produced. Only those that were volatile at 400°K found their way into the sampling tube. Compounds of high molecular weight remained on the catalyst in the reaction vessel and were recovered only after the end of the experiment. The fractionation between this "wax" fraction and CO_2 was 61 per mil in the first experiment, some 10 per mil greater than the C_{2+}-CO_2 fractionation. Unfortunately the wax fraction in experiment 2 was too small for isotopic analysis.

It thus appears that the Fischer-Tropsch reaction gives a carbon isotope fractionation of the same sign and magnitude as that observed in meteorites. Although our results thus strengthen the case for catalytic synthesis of the organic compounds in meteorites, they also place additional constraints on the model.

On the basis of the observed fractionation between "wax" and CO_2 at 400°K, the organic compounds in type II carbonaceous chondrites may have formed at ~400°K and those in type I carbonaceous chondrites at a slightly lower or higher temperature, with the exact temperature dependent on the temperature coefficient of the kinetic isotope effect. This value is in good agreement with previous estimates (*15*), based on trace element content and the formation temperatures of certain minerals in carbonaceous chondrites (Fe_3O_4, 400°K; hydrated silicates, ~350°K). However, in a cooling solar nebula it may be difficult to keep most of the carbon in the form of CO down to such low temperatures. Although CO is the stable form of carbon at high temperatures, it becomes unstable with respect to hydrogenation (Fischer-Tropsch) reactions at lower temperatures. Thermodynamically, the most favored product is CH_4; the next most favored product is ethane, then benzene, and other hydrocarbons. Thus, if equilibrium were maintained, most of the CO would be converted to CH_4 before formation of heavier hydrocarbons became possible. (Their formation temperatures lie some 100° to 150° below those of methane.) At total pressures of 10^{-4} and 10^{-5} atm, only 1 percent of the carbon would remain in the form of CO by the time the temperature had dropped to 570° and 520°K. Essentially no CO would be left at 400°K.

This dilemma does not seem to be insoluble. Hydrogenation of CO is known to be very slow in the absence of a suitable catalyst. The fact that carbon compounds are abundant only in meteorites containing magnetite and hydrated silicates may mean that these compounds themselves were the required catalysts. Above the formation thresholds of these minerals (400°K and ~350°K) lack of a catalyst may have permitted the survival of CO. In support of this suggestion, there is some evidence that the solar nebula cooled rapidly from high temperatures down to the accretion range of meteorites, and then much more gradually (*16*). For the ordinary chondrites, the accretion range was a 100-degree interval centered on 510^{+80}_{-60}°K (*17*). For the carbonaceous chondrites, this range seems to have been ~300° to ~400°K (*15*). No carbonaceous chondrites without magnetite are known, which suggests that accretion in the source region of carbonaceous chondrites commenced only below 400°K. Presumably the range above 400°K was traversed too rapidly for any significant accretion to take place.

Formation of hydrated silicates may also have provided the cations needed for the carbonate. These silicates, although mineralogically ill-defined (*18*), have a distinctly lower cation-to-silicon ratio than the olivine from which they seem to be derived (*2, 15*). In a gas of cosmic composition at a total pressure of 10^{-4} atm, formation of hydrated silicates is expected to commence below about 350°K (*15*). The following equations schematically represent the process:

$$12(Mg,Fe)_2SiO_4 + 14H_2O \rightarrow 2Fe_3O_4 + 2H_2 + 3(Mg,Fe)_6(OH)_8Si_4O_{10} \quad (3)$$

$$4(Mg,Fe)_2SiO_4 + 4H_2O + 2CO_2 \rightarrow 2(Mg,Fe)CO_3 + (Mg,Fe)_6(OH)_8Si_4O_{10} \quad (4)$$

Just as in terrestrial serpentinization reactions (*19*), some basic cations are left over. The excess cations can appear either as magnetite (Eq. 3) or carbonate (Eq. 4). Basic oxides react rapidly with CO_2 and would thus remove it from the gas phase fast enough to prevent secondary reactions or isotopic equilibration.

Alternatively, the organic polymer in meteorites may have a formation temperature close to that of methane. Thermodynamic calculations (*20*) have shown that aromatic polymers may become the favored product under a variety of conditions. Moreover, an essential first step in the Fischer-Tropsch synthesis is adsorption of CO on the surface of the catalyst. At the low partial pressures of CO expected in the solar nebula (10^{-7} to 10^{-8} atm), it is conceivable that effective adsorption may not commence until temperatures have fallen low enough to permit the formation of products other than methane.

Our experiments also provide a very tentative clue to the initial isotopic composition of the carbon in the nebula. Carbonaceous chondrites contain only about 6 percent of their cosmic complement of carbon; the remainder was presumably left behind in the nebula as compounds of low molecular weight. Assuming that CO was the sole starting compound, and comparing the CO_2-CO-wax fractionation in our experiments with the polymer-carbonate fractionation in type II carbonaceous chondrites, we would estimate an initial carbon composition of +15 per mil on the PDB scale. This is remarkably close to the isotopic composition of carbon in lunar soil (*21*), which is a mixture of indigenous, meteoritic, and solar-wind carbon.

MICHAEL S. LANCET
EDWARD ANDERS

Enrico Fermi Institute and *Department of Chemistry, University of Chicago, Chicago, Illinois 60637*

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