An NMR Study of the Mode of Incorporation of Ethene into Propene in the Fischer–Tropsch Reaction over Cobalt

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Incorporation of added ethene into the propene fraction formed by the Fischer–Tropsch reaction over cobalt supported on Al metal has been studied. Either the CO or the C_2H_4 in the feed gas was labeled with ^{13}C, and the products were studied by ^{13}C NMR spectroscopy. All of the propene isotopomers which contain the ^{13}C label could be identified. The formation of products which contain a single-labeled atom from the (doubly labeled) ethene feed was observed; this required that some of the ethene dissociate to C_1 fragments. Among doubly labeled propenes, there was a strong preference for those isotopomers with the labels on adjacent carbon atoms. This could best be accounted for by a model which assumes that some ethene incorporation occurs as a C_2 unit. The spectra gave no evidence that two C_1 units, one from CO and one from ethene, recombine to give C_2H_4 in the product mixture. © 1990 Academic Press, Inc.

INTRODUCTION

The incorporation into products of the Fischer–Tropsch (F–T) synthesis of ethene (or other alkenes) added to the conventional feed gas mixture was first reported by Smith, Hawk, and Golden in 1930 (*1*). Occasional studies of the effects of added alkenes have appeared since then, with the ethene C_2 unit variously claimed to be incorporated intact or as separate C_1 units (*2, 3*). The results of these investigations have been reviewed briefly (*4*). The question of ethene incorporation as C_2 units or as C_1 fragments has never been settled. Some of these studies have been carried out with ^{14}CO labeling of the feed gas, appropriate chemical degradation of products, and determination of radioactive decay in the fragments to locate label in the product carbon chains (*5*). In other cases, MS has been used to determine the number of ^{13}C-labeled carbon atoms incorporated into product molecules. In favorable cases the location of label atoms within a carbon chain can also be determined by careful interpretation of the mass spectrum (*6*). None of the methods used in these studies can give di-rect information on the location of labels in product carbon chains.

A good many NMR studies of adsorbed species on catalyst surfaces have been reported. NMR has been much less used to investigate the products of catalytic reactions. Deuterium NMR has been used together with MS to identify the products of the catalyzed exchange of deuterium with cyclopentane (*7*). We have found only a few cases in which this method has been used to locate ^{13}C labels in a product carbon chain. Mims and McCandlish (*8*) used proton NMR to locate ^{13}C atoms ($I = \frac{1}{2}$) from ^{13}CO in the butene-1 product by observing the $J_{^{13}C-^{1}H}$ coupling shown by protons attached to the labeled carbon. A very recent publication (*9*) (of which we were unaware during the course of the work reported here) describes the use of ^{13}C NMR to obtain detailed isotope distributions in C_3 and C_4 reaction products. There are advantages in using ^{13}C NMR for the direct determination of the labeled positions. The chemical shift range for carbon is much greater than for protons, so line separations are large and assignment of lines is usually more certain. ^{13}C signals can also be used to identify the

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locations of deuterium labels by their three-fold splitting and isotope shift. Disadvantages in the use of ^{13}C NMR are the lower sensitivity (compared to protons) and possible distortion of line intensities by the nuclear Overhauser effect which arises from attached protons.

We report here a study of the mode of incorporation of ethene into F–T products using ^{13}C-labeled feeds, and ^{13}C NMR for the identification and location of labels in the products. Propene was selected as the product for intensive investigation because the double bond identifies the atoms in the carbon chain of this molecule and because the three line sets for these carbon atoms are clearly isolated in the ^{13}C NMR spectrum of the product mixture. The results give a definitive answer to the question of incorporation as C_2 or as two C_1 units over the Co catalyst used.

EXPERIMENTAL

Preparation of catalyst. Al tubing 6.5 cm long and 0.65 cm o.d. was cleaned by etching in 6 M HCl, rinsed in distilled water, and immersed immediately in 30 ml of 0.2 M Co(II) nitrate solution. The tubing was made the cathode of an electrolysis cell and 0.0128 g Co metal deposited on the outside only at a current of 0.2 A for 60 s, and then at 1.0 A for 30 s. (The reduction at programmed current density is necessary to obtain an adherent Co layer.) Support and catalyst were washed with H_2O, then with acetone, and again with H_2O. The Co was activated by heating in a stream of H_2 (flow rate 20 ml/min) for 30 min at 120°C and another 60 min at 360°. It was stored in the reactor under flowing H_2 at 240°C between runs. Activity over weeks of use (by analysis of F–T product composition and yields) was constant within 5% when the catalyst was reduced between runs in H_2 (20 ml/min) for 1 h at 360°C. Minimum thickness of the Co layer (if close-packed, and ignoring porosity) is 0.0001 cm, estimated from the current passed during electrolysis and density of Co metal. Catalysts deposited elec-

trolytically on Cu or stainless steel had lower activity, as did catalysts deposited on Al from solutions of chloride or sulfate salts of Co(II).

Characterization of catalyst. Nitrogen physisorption measured by the BET flow method (*10*) gave the surface area 126 m^2/g (Co catalyst weight only). Hydrogen chemisorption measured by the static method (*11*) gave the area 122 m^2/g. The consistency of these surface area values implies that the atoms on the catalyst surface are essentially all active Co. The calculated dispersion is 7.5%. Reactivity was routinely measured at 240°C and 1 atm pressure with a 3 : 1 ratio of H_2 : CO feed gas. For the reactivity check, products were fractionated by carbon number using GC and these fractions analyzed for unsaturation and chain branching by NMR. F–T products follow the Schultz–Flory distribution (with methane high and the C_2 fraction low) (*12*) through the C_6 fraction (one mole% of product, which is our detection limit), with $\alpha = 0.72$. When ethene was added to the feed gas, the Schultz–Flory correlation line moved upward and its slope decreased with $\alpha = 0.77$, reflecting greater production of higher molecular weight products. We have no means to determine the presence or thickness of any oxide layer between the Al support and the Co catalytic surface; this was not done.

Conditions for reactions with added ethene. A single pass reactor supported vertically and operated in the differential mode held the cylindrical catalyst and support. Reactions normally were conducted at a total downward gas flow rate of 20 ml/min (measured at STP) against atmospheric pressure, with the reactor heated to 240°C. The thermocouple and its support effectively limited gas flow to the annular space between catalyst and reactor wall. Residence time within this volume was 8.8 s. Premixed 3 : 1 H_2 : CO was passed through the system, and ethene introduced to this flowing gas stream at the rate of 0.40 ml/min with a syringe pump. Thus, the input

gas stream consisted of 2 mole% ethene, 24.5 mole% CO, and 73.5 mole% H_2. Total conversion was in the range 3–4%. Double-labeled (99% ^{13}C) $^{13}C_2H_4$ was purchased from Cambridge Isotope Laboratories. ^{13}CO (99% label) was purchased from Isotec Laboratories.

Effluent gas from the reactor was passed through three traps in series held at $-78°C$. Each trap contained 1.5 ml of 3 : 1 (volume ratio) $CH_2Cl_2 : DMSO-d_6$. Under these conditions, about 20% of the C_3 hydrocarbons in the gas stream are not retained in two traps; three traps retain essentially all of this fraction. CO, H_2, and CH_4 are not retained. The C_2 fraction is partly retained. Collection of sample from a single run was normally carried out for 30 min of steady-state operation.

Recording NMR spectra. The solutions retained in the three traps were combined and transferred to a 10-ml NMR tube. Spectra were recorded on a Bruker WP-400 spectrometer operated at 100.6 MHz for ^{13}C, with a 90° pulse. Maximum field is desirable for the increased sensitivity it offers; the isolation of propene line sets is still adequate at lower fields. The DMSO-d_6 solvent provided the deuterium lock. NOE was suppressed by a pulse sequence (INVGATE: decoupler off for 5-s delay; decoupler on through 90° pulse, 41.25-μs delay, record FID) which turns off the proton decoupler during a delay prior to the exciting pulse. Saturation was avoided by the addition of an iron complex, which reduced relaxation times to ca. 0.5 s from the normal range of 20–30 s (*13*). In order to obtain adequate signal/noise ratios, samples generally were run overnight, with signal averaging over 6000–8000 pulses.

Under the conditions given, with solute concentrations up to the order of 0.0002 *M* for the abundant species, only ^{13}C-labeled sites are observed. Signals from ^{13}C natural abundance in the solutes are not detected. Thus, all ^{13}C NMR lines originate with the labeled ^{13}CO or the $^{13}C_2H_4$ introduced with the feed gas.

The chemical shift scale used is referenced to the ^{13}C signal of external TMS in a concentric capillary. This gives the chemical shift of the center line of the DMSO-d_6 pattern as 41.0 ppm. This value differs considerably from the nominal tabulated value for DMSO-h_6 at 39.5 ppm, which would place the DMSO-d_6 pattern at 38.6 ppm after the correction of 0.9 ppm for the isotope shift. Fresh mixed solvent without added spin relaxer gives the DMSO-d_6 pattern center at 40.1 ppm vs external TMS. The value observed is quite sensitive to solvent composition and to solute concentration. A reliable external reference is necessary since our samples are in the mixed solvent already described and variations in the CH_2Cl_2–DMSO ratio could affect the position of an internal reference line.

These samples in polyethylene-capped NMR tubes are not fully stable: dissolved hydrocarbons diffuse out significantly within a few days at room temperature or within weeks at refrigerator temperature. Consequently, all samples were stored at 0–5°C until the NMR spectra were recorded, and this was done promptly. We assume that neither the slow evaporation nor the trapping procedure fractionates isotopomers of a given molecular species.

RESULTS

Product composition as total mole% at a given carbon number was measured by calibrated GC, with the results: 76.3% C_1, 7.0% C_2, 9.0% C_3, 4.2% C_4, 2.4% C_5, and 1.1% C_6. The compositions of the lower fractions formed from ^{13}CO and H_2, and thus fully labeled, were determined ($\pm 5\%$) by NMR: C_2 at 46% ethane and 54% ethene; C_3 at 38% propane and 62% propene; and C_4 at 36% butanes and 64% butenes.

The NMR spectra obtained from these samples are very rich in lines due to the substantial number of reaction products (all hydrocarbons; weak lines due to carbinol carbon atoms may be concealed under the very intense solvent lines and sidebands)
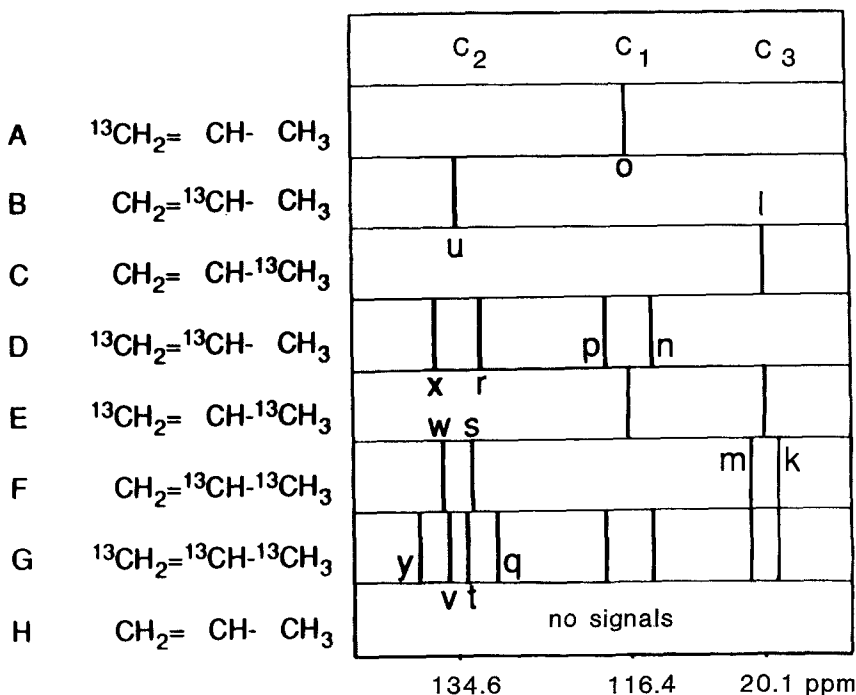
FIG. 1. Capital letters A through H assigned to designate the eight possible isotopomers of propene, and stick plots of the ^{13}C NMR spectra they produce. Individual lines are designated by the lower-case letters k through y.

and their isotopomers. However, the line sets for all three carbon atoms of propene are relatively isolated on the chemical shift axis, and we interpret here the data for that compound obtained without separation of the product mixture. (Higher hydrocarbons could be treated in equal detail after a preliminary separation by GC, but the results are limited by overlapping lives.) If we limit consideration to propene, the eight possible isotopomers and the contributions of each to the ^{13}C NMR pattern are given in Fig. 1. A total of 15 lines is possible if we neglect the small 1–3 coupling. These lines are designated by the lower-case letters k through y indicated in the figure. Note that each product gives a unique pattern. The carbon–carbon coupling constants observed are: $J_{1-2} = 69$ Hz, $J_{1-3} = 4$ Hz, and $J_{2-3} = 42$ Hz. The experimental NMR pattern for each carbon atom may not be symmetrical as they are drawn in Fig. 1, due to the small isotope shifts of ^{13}C signals in isotopomers

with one or more ^{13}C atoms adjacent to the ^{13}C which is the source of the signal.

In order to assign relative yields of the eight isotopomers, relative intensities (proportional to areas) of the NMR lines are required. Direct integration would be tedious and imprecise; instead we use the approximation that areas are proportional to peak heights if linewidths are constant. The measured linewidths fall in the range 2.0 to 2.5 Hz (full width at half height). Thus, the measured peak heights collected in Table 1 can be used with the relationships given in Table 2 to evaluate relative concentrations of the species A–G.

Reactions were studied with two different sources of label in the feed gas. Reaction 1 used unlabeled ^{12}CO and double-labeled $^{13}C_2H_4$. Reaction 2 used labeled ^{13}CO and unlabeled $^{12}C_2H_4$:
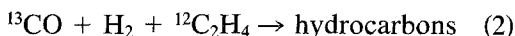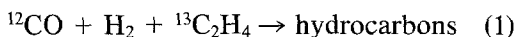
$$^{12}CO + H_2 + {}^{13}C_2H_4 \rightarrow \text{hydrocarbons} \quad (1)$$

$$^{13}CO + H_2 + {}^{12}C_2H_4 \rightarrow \text{hydrocarbons} \quad (2)$$

TABLE 1

Heights of Propene Lines in Isotopomer Mixtures
Produced by Reactions 1 and 2[a]

Line Symbol	Reaction 1	Reaction 2
k	12.0	13.6
l	12.8	7.1
m	11.1	11.3
n	8.1	16.3
o	10.8	8.2
p	9.5	14.6
q	2.4	8.4
r	4.6	2.2
s	5.1	2.1
t	2.6	8.1
u	9.4	1.7
v	2.7	8.9
w	5.0	2.2
x	4.2	2.6
y	2.7	9.7

[a] Peak heights given in centimeters. Reactions run at 20 ml/min gas flow rate 240°, and 1 atm pressure.

Typical NMR spectra of the isotopomer mixtures which make up the propene fractions from these two reactions are given in Fig. 2. Note that line positions are the same in both mixtures, while their relative intensities differ substantially.

We assume that the mechanisms by

TABLE 2

Product Concentrations from NMR Line Intensities

Product		Concentration[a]
A	$^{13}CH_2 = CH - CH_3$	$B = u$
B	$CH_2 = {}^{13}CH - CH_3$	$D = (r + x)$
C	$CH_2 = CH - {}^{13}CH_3$	$F = (s + w)$
D	$^{13}CH_2 = {}^{13}CH - CH_3$	$G = (q + t + v + y)$
E	$^{13}CH_2 = CH - {}^{13}CH_3$	$(A + E) = o$
F	$CH_2 = {}^{13}CH - {}^{13}CH_3$	$(C + E) = l$
G	$^{13}CH_2 = {}^{13}CH - {}^{13}CH_3$	$(D + G) = (n + p)$
H	$CH_2 = CH - CH_3$	$(F + G) = (k + m)$

[a] Concentrations of products A through H are measured relative to the concentration of G in terms of intensities of lines k–y. All symbols are defined in Figure 1.

which CO and ethene participate in hydrocarbon formation are independent of the carbon isotopes in these reactants. In that case, we can expect the following reciprocal relationships, where A1 means "the amount of A formed by Reaction 1", and F2 means "the amount of F formed by Reaction 2." These relationships reflect the expectation that ^{12}CO and ^{13}CO will participate in Reactions 1 or 2 by the same mechanism and at the same rates, if we neglect any kinetic isotope effects. Correspond-
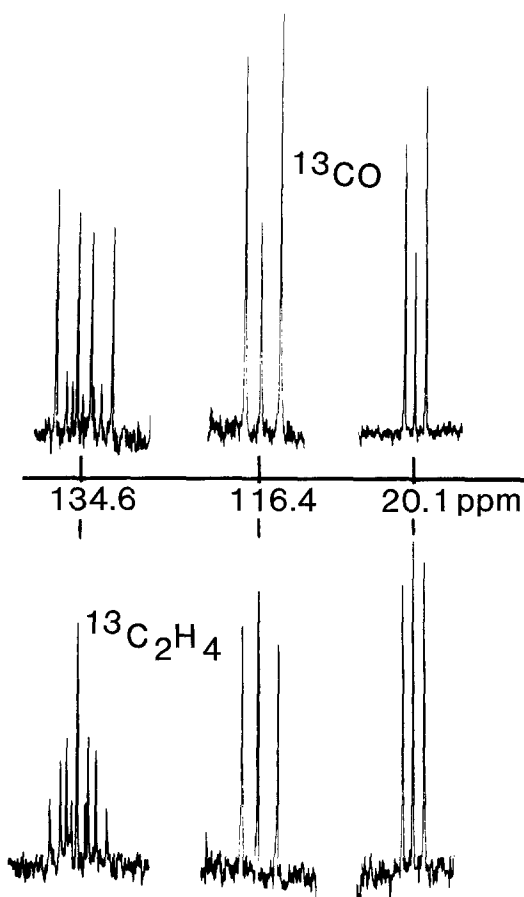

FIG. 2. NMR patterns observed for the three carbon atoms of propene in the isotopomer mixtures produced by the reactions with added ethene. Lower traces: products from Reaction 1, with $^{13}C_2H_4$ label. Upper traces: products from Reaction 2, with ^{13}CO label. Both spectra were recorded after reaction at total gas flow rate 20 ml/min, using 24.5 mole% CO, 73.5 mole% H_2, and 2 mole% C_2H_4.

ingly, $^{13}C_2H_4$ and $^{12}C_2H_4$ will participate at the same rates. The result is that carbon chain positions which are labeled in Reaction 1 are unlabeled in products of Reaction 2, and vice versa.

$$A1 = F2 \qquad E1 = B2$$
$$B1 = E2 \qquad F1 = A2$$
$$C1 = D2 \qquad G1 = H2$$
$$D1 = C2 \qquad H1 = G2$$

In the two "mole% found" columns of Table 3 we collect the calculated amounts of labeled propene products found in Reactions 1 and 2 conducted under the same conditions except for the source of label and at gas flow rates of 20 ml/min. Note that this table lists products formed in Reactions 1 and 2 from the same reactants (but with different labels) on the same line. Consequently, particular isotopomers designated by the letters A–H appear in a different order in the two product columns.

Calculation of the product distributions

TABLE 3

Propene Isotopomer Distributions from Reactions 1 and 2 at 20 ml/min Gas^a Flow Rate, 240°C, 1 atm Pressure

Reaction 1: $^{12}CO + {}^{13}C_2H_4 + H_2$		Reaction 2: $^{13}CO + {}^{12}C_2H_4 + H_2$	
Product	Mole% found	Mole% found	Product
A^b	6.8^c	6.2^c	F^b
B	7.8	8.1	E
C	6.9	7.0	D
D	7.2	7.9	C
E	2.6	2.5	B
F	8.3	7.8	A
G	8.5	8.7	H
H	51.9	51.6	G

^{a} Gas contained 2 mole% ethene, 24.5 mole% CO, and 73.5 mole% H_2.

^{b} Products A–H are identified in Fig. 1. The reciprocal relations described in the text are not followed exactly because the normalization is to $G1$ in Reaction 1 and to $G2$ in Reaction 2.

^{c} Repeatability in calculation of these entries from measured peak heights estimated to be ±8%.

listed in Table 3 involves the following steps:

a. Evaluate directly the relative amounts formed of B, D, F, and G, and the combinations $(A + E)$, $(C + E)$, $(D + G)$, and $(F + G)$ from the relationships in Table 2.

b. Use G as the reference to express the relative amounts formed as B/G, D/G, etc.

c. There are no explicit expressions in Table 2 for A, C, and E. Use the reciprocal relations

$$A1 = F2, C1 = D2, \text{ and } E1 = B2$$

to solve for A/G, C/G, and E/G.

d. The unlabeled isotopomer H is not observed by NMR, but can be estimated by the reciprocal relation $H1 = G2$. The intensities in Reactions 1 and 2 are independently normalized to $G1$ and $G2$. It is thus necessary to evaluate an intensity factor to relate amounts formed in the two sets of reactions. This is taken as the ratio of the total concentration from each reaction of products which contain only a single atom from ethene. Thus we have

$$H1 = G2 (A1 + B1 + C1)/(D2 + E2 + F2).$$

Measurements of line intensities on duplicate spectra recorded under the same conditions give a 95% confidence interval of ±5% for the heights of average and stronger lines. For the weakest (height < 2 cm) lines, this error rises to ±10%. These statements conceal a larger source of potential errors: while the lines within sets produced by the individual carbon atoms have the correct relative intensities, lines from two sets produced by different carbon atoms may not. Thus, the two possible expressions from Table 2 for $(D + G)$, equal to $(r + x) + (q + t + v + y)$ or to $(n + p)$, give values which can differ by much more than the estimated reproducibility of line intensities. This is also true for the two possible expressions for $(F + G)$. These random differences arise because lines n, o, p originate with C_1, and lines k, l, m with C_3, and their intensities are not directly comparable

with those of lines q–y from C_2. We have circumvented this problem by using only *ratios* of line intensities within these sets in calculating the data in columns 2 and 3 of Table 3. The ratios used were $(A + E)/(D + G) = o/(n + p)$, and $(C + E)/(F + G) = 1/(k + m)$. Consequently the (unknown) factors which correct intensities of lines due to C_1 or C_3 to those due to C_2 cancel. The result is that the repeatability of results in Table 3 is about ±8% for calculations carried out independently on different line intensity data. Another result of this method for handling the calculations is that the apparent redundancies in the data in Table 2 are lost because they cannot all be used for these calculations.

We understand some, but probably not all, of the reasons for these intensity variations. The NMR lines for the propenes appear over a chemical shift range of 120 ppm, and it is impossible to phase correct the spectrum equally well throughout this range. In fact, the corrections were applied separately to the two sections of the spectrum upfield and downfield from the intense solvent lines at $\delta = 40$–55 ppm, and this must also contribute to intensity differences. Baseline roll which originates in the intense solvent peaks is never completely eliminated. Residual differences in relaxation times for the three carbon atoms also may contribute. It is not yet clear how fully these problems can be eliminated.

DISCUSSION

It is evident from Table 3 that the reciprocal relationships are obeyed. Furthermore, the mole% of products $A1$, $B1$, and $C1$ and of $D2$, $E2$, and $F2$ are approximately equal. We conclude that incorporation of a $^{13}C_1$ unit formed from $^{13}C_2H_4$ (or of $^{12}C_1$ from $^{12}C_2H_4$ in reaction 2) is equally probable at each of the propene carbon atoms. The other two carbon atoms in these products must come from ^{12}CO (Reaction 1) or from ^{13}CO (Reaction 2), presumably as monomeric units.

We consider now the molar abundances of $D1$, $E1$, $F1$ and $A2$, $B2$, $C2$, which are decidedly unequal within these sets. In Reaction 1, the single ^{12}C in D, E, or F must originate from ^{12}CO, while in Reaction 2 the single ^{13}C must originate from ^{13}CO. In both sets of products, there is a strong preference for those products with adjacent carbon atoms which originate from ethene: $^{13}C_2$ at positions 1,2 or 2,3 from Reaction 1, and $^{12}C_2$ at positions 2,3 or 1,2 from Reaction 2. In both cases the carbon isotope in these positions *must* come from ethene, and it may originate with an intact C_2 unit.

The data indicate equal probabilities for the double bond to be found between two ^{13}C atoms (in $D1$) or between one ^{13}C and one ^{12}C (in $F1$). In Reaction 2, the corresponding products are $A2$ and $C2$. These results suggest that the double bond is not fixed during growth of the C_3 chain. Instead, we infer that release of the C_3 unit from the catalyst surface requires one or more shifts of hydrogen atoms to form propene. These shifts occur so that formation of the double bond found in the product occurs with equal probabilities at the two ends of the C_3 chain.

The ^{13}C NMR line due to excess ethene or to recombination of two $^{13}C_1$ units, which would contribute to the same line, appears at 123.9 ppm when $^{13}C_2H_4$ is added to the feed gas. We have searched for the corresponding line in products of Reaction 2, where $^{12}C_1$ from ethene might recombine with $^{13}C_1$ from ^{13}CO to produce singly labeled ethene. There is no line for this product. Thus there is no evidence for combination of C_1 units from the two carbon sources to form ethene. Labeled $^{13}C_2H_6$ is formed in large amounts (46% of C_2 fraction) in Reaction 1, presumably by reduction of $^{13}C_2H_4$ feed. Smaller amounts are formed by combination of $^{13}C_1$ units from ^{13}CO in Reaction 2, but the major amount of unlabeled C_2H_6 of course is not detected by NMR.

This study has provided eight data points on the distribution of reaction products obtained under one set of reaction conditions; these impose too few constraints on the

system to draw reliable conclusions by kinetic modeling. We do not know whether the C_1 units from C_2H_4 and from CO are kinetically the same or different. We have no data on the relative probabilities of chain initiation and propagation by C_1 or C_2 units. Most of these cases would require the determination of more rate constants by optimizing the fit to distribution of reaction products than we have data points. Reliable kinetic modeling thus seems out of the question.

Full analysis of the butenes produced cannot be carried out because of overlap lines within some of the NMR line sets which originate with *cis* and *trans*-2-butene. The partial analysis completed requires, as in the case of the propenes, that some ethene be incorporated as C_1 units and some as C_2 units.

We have not discussed these results in terms of any mechanistic model for reactions at the catalyst surface. We see no contradiction between any of these data and the widely accepted carbide mechanism for the F–T reaction.

CONCLUSIONS

The conclusions below are consistent with the currently accepted carbide theory for the mechanism of the Fischer–Tropsch reaction.

1. Ethene *must* dissociate in part to surface C_1 units which can be incorporated individually in a growing carbon chain.

2. Ethene is incorporated in part as C_2 units. This may imply that some ethene reacts without prior dissociation (the simplest explanation), but it may also result from inability of the two C_1 units to move apart on the catalyst surface, with the consequence that chain growth preferentially incorporates two monomer units which were formed from the same absorbed C_2H_4.

3. Incorporation of single C_1 units from ethene is equally probable at the three carbon positions of the propene eventually formed.

4. Labeling of feed gases with $^{13}C_1$, followed by product analysis by ^{13}C NMR, gives site-specific information about the incorporation of reactants into reaction products. The technique can give answers to specific questions about reaction mechanisms when it is possible to study them by ^{13}C-labeling.

REFERENCES

1. Smith, D. L., Hawk, C. O., and Golden, P. L., *J. Amer. Chem. Soc.* **52**, 3221 (1930).
2. Golovina, O. A., Sakharov, M. M., Roginskii, S. Z., and Dokukina, E. S., *Russ. J. Phys. Chem.* **33**, 471 (1959).
3. Pichler, H., and Schulz, H., *Chem. Ing. Tech.* **42**, 1162 (1970).
4. Morris, S. R., Moyes, R. B., Wells, P. B., and Wyman, R., *J. Catal.* **96**, 23 (1985).
5. Eidus, Y. T., *Russ. Chem. Rev.* **36**, 338 (1967).
6. Corolleur, C., Corolleur, S., and Gault, F. G., *J. Catal.* **24**, 385 (1972).
7. Brown, R., and Kemball, C., *J. Catal.* **104**, 480 (1987).
8. Mims, C. A., and McCandlish, L. E., *J. Amer. Chem. Soc.* **107**, 696 (1985); Mims, C. A., and McCandlish, L. E., *J. Phys. Chem.* **91**, 929 (1987); Mims, C. A., *Catal. Lett.* **1**, 293 (1988).
9. Mims, C. A., McCandlish, L. E., and Melchior, M. T., *Proc. Int. Congr. Catal.* **4**, 1992 (1988).
10. Nelsen, F. M., and Eggerstein, F. T., *Anal. Chem.* **30**, 1387 (1958).
11. Revel, R. C., and Bartholomew, C. H., *J. Catal.* **85**, 63 (1984).
12. Schultz, G. V., *Z. Phys. Chem. B* **29**, 299 (1935); Flory, P. J., *J. Amer. Chem. Soc.* **58**, 1977 (1936).
13. Levy, G. C., and Cargioli, J. D., *J. Magn. Reson.* **10**, 231 (1973).