The slope is less than one because the ^{14}C alkanes formed during the period of ^{14}C ethene addition are diluted by the alkane accumulation in the CSTR during the course of the run; hence, higher carbon number alkanes accumulate to a greater extent than lower carbon number alkanes and thereby cause the slope to be negative. The slope of the line defined by the C_{16} - C_{21} alkanes is positive as expected if ^{14}C labeled ethene is incorporated randomly into the growing chain (case IV, figure III-9).

Again, the slope is less than unity because of accumulation of higher carbon number alkanes in the CSTR that were formed from unlabeled CO prior to the ^{14}C addition period.

III-I. Results from Adding Labeled Alcohols to the Syngas

Labeled 1-pentanol was converted in a CSTR at 7 atmospheres using the C-73 catalyst, ca. 10% Fe supported on high surface area silica and an unsupported iron catalyst promoted by ca. 6% ThO_2. It can be seen from the data in figure III-53 that the activity of the alkane fraction from each catalyst exhibits a similar behavior, and the activity decreases with increasing carbon number. Because an accurate measure of the accumulation of unlabeled materials was not obtained, a definitive conclusion cannot be reached about the significance of the slope of each line. These slopes are: ThO_2-Fe, -0.13; C-73, -0.19 and Fe-SiO_2, -0.26.

The activity of the alkene components from two runs was determined (figures III-54 and III-55). In the run with the 6% ThO_2-Fe catalyst, the alkenes have a higher activity per mole than the corresponding carbon number alkane. Furthermore, the slope of the alkene curve (-0.22) is higher than for the alkane curve (-0.13). This, while apparently clear-cut, is not what was observed with other catalysts where the slope of the alkene curve was smaller than for the alkane line. For the run with the C-73 catalyst the situation is much less clear-cut. The data in figure III-55 does not have activity for many common carbon number compounds; if the alkene line is extrapolated the pattern would be similar to that shown in figure III-54. Unfortunately, when the measurements were made, it was not apparent that the accumulation factor would impact so severely the ^{14}C tracer data. While the data illustrates the uniqueness of the ^{14}C tracer technique to elucidate this accumulation factor, it was not apparent until near the end of the contract period.

Gaseous product activities from the conversion of CO/H_2 containing labeled 1-pentanol with the 6% ThO_2-Fe catalyst are shown in figure III-56. It is apparent that a detectable amount of hydrogenolysis to C_1 - C_4 hydrocarbon products did not occur. Again, it is noted that the CO_2, but not CO, contained ^{14}C. The heavier hydrocarbons were not sufficiently volatile to permit us to conclude whether the activity in the $C_5{}^+$ alkane plus alkene fraction is constant with increasing carbon number.

In order to verify the observations made with labeled 1-pentanol, 1-hexanol [2-^{14}C] was synthesized and added to the syngas feed to a CSTR containing a C-73 catalyst and operated at 262°C and 7 atm. In this case, the data are also consistent with hydrogenolysis being less than could be detected and with some decarbonylation (figure III-57). In this case, it appears that decarbonylation was at about 50% of the amount of alcohol incorporation. The much more extensive dilution of the $^{14}CO_2$ from the

Figure III-53. ^{14}C activity in alkane fraction of products for ^{14}C labeled pentanol in the syngas feed to C-73 (○), 10% Fe-SiO$_2$ (△) and 6% ThO$_2$-Fe (□) catalyst (CSTR, 262°C, 7 atm.).

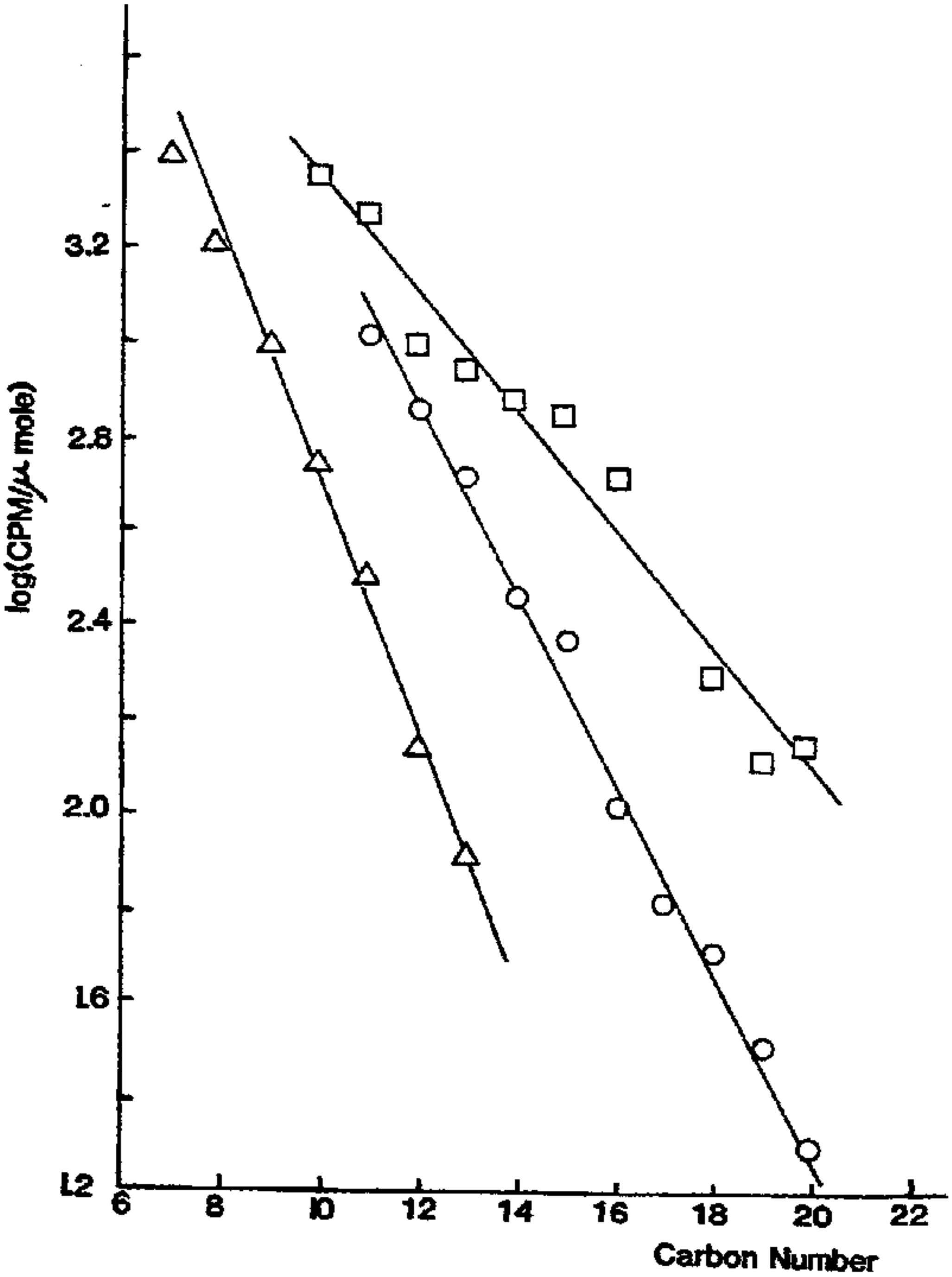
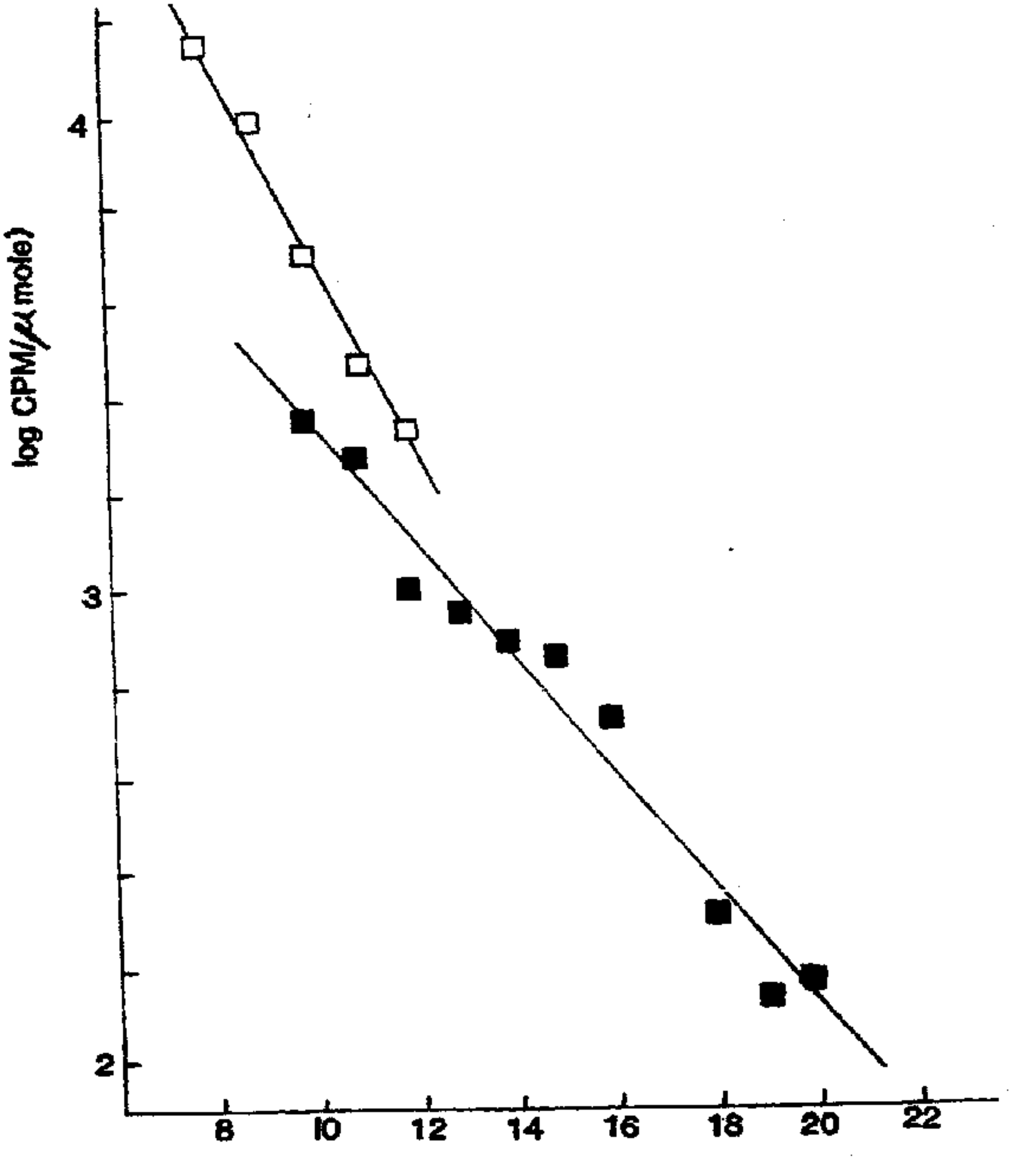


Figure III-54. The ^{14}C activity for the alkene (○) and alkane (■) products produced when 1-pentanol[1-^{14}C] was added to the syngas feed to a 6% ThO_2-Fe catalyst (CSTR, 262°C, 7 atm.).



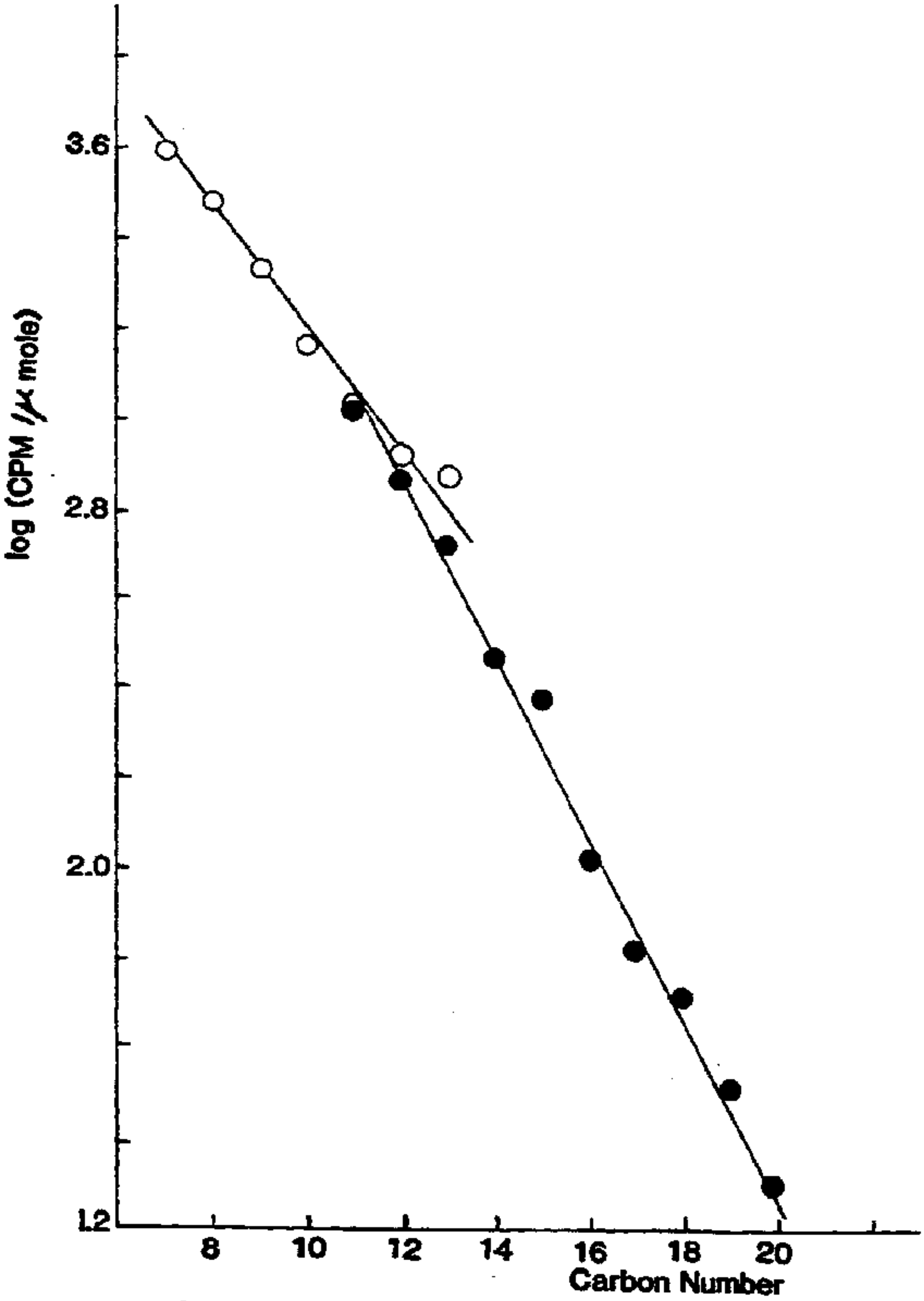


Figure III-55. The ^{14}C activity for the alkene (○) and alkane (●) products produced when 1-pentanol[1-^{14}C] was added to the syngas feed to a C-73 catalyst (CSTR, 262°C, 7 atm.).

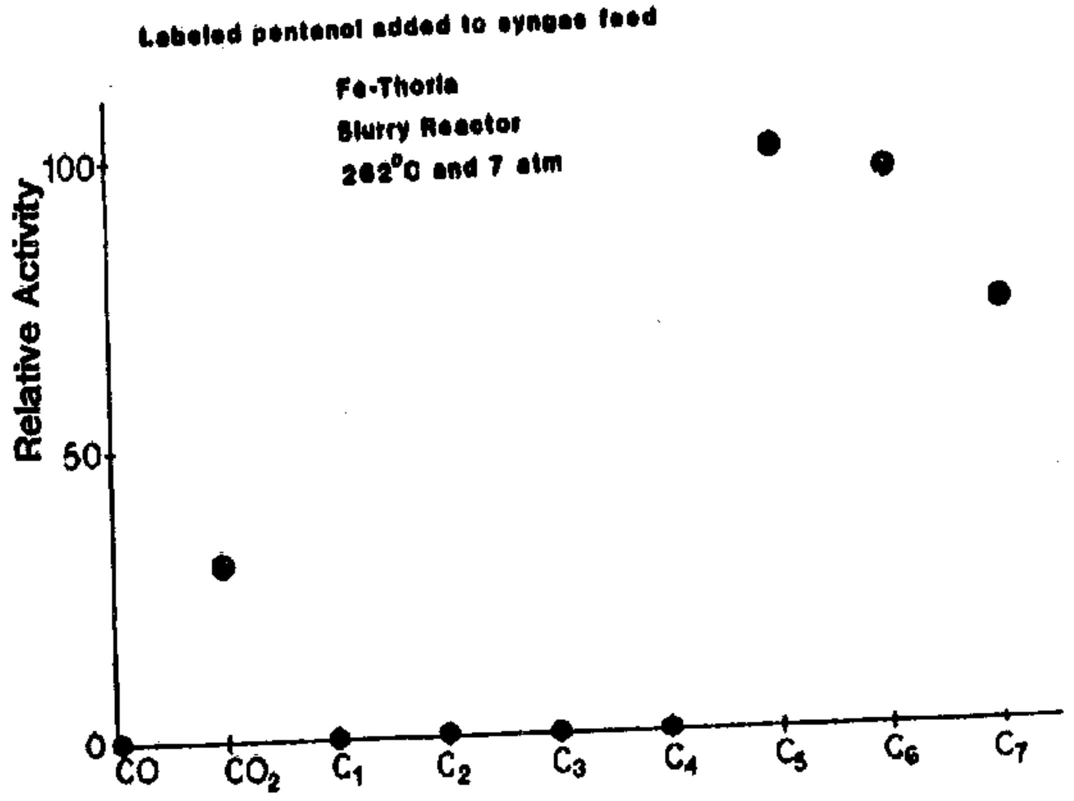


Figure III-56. Relative C-14 activity ($C_5 = 1.0$) in gaseous products when labeled 1-pentanol was added to the syngas feed to a 6% ThO_2-Fe catalyst (CSTR, 262°C, 7 atm.).

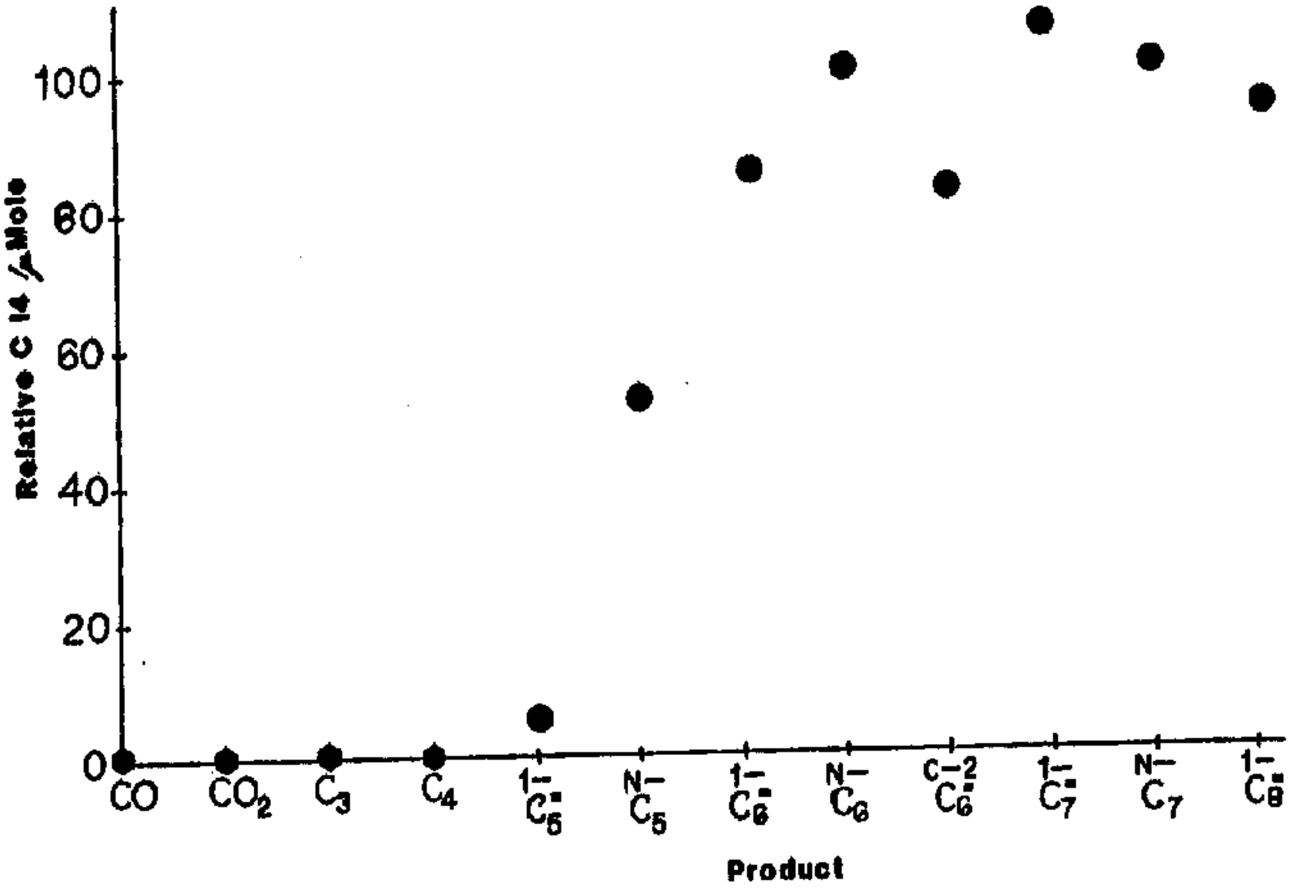
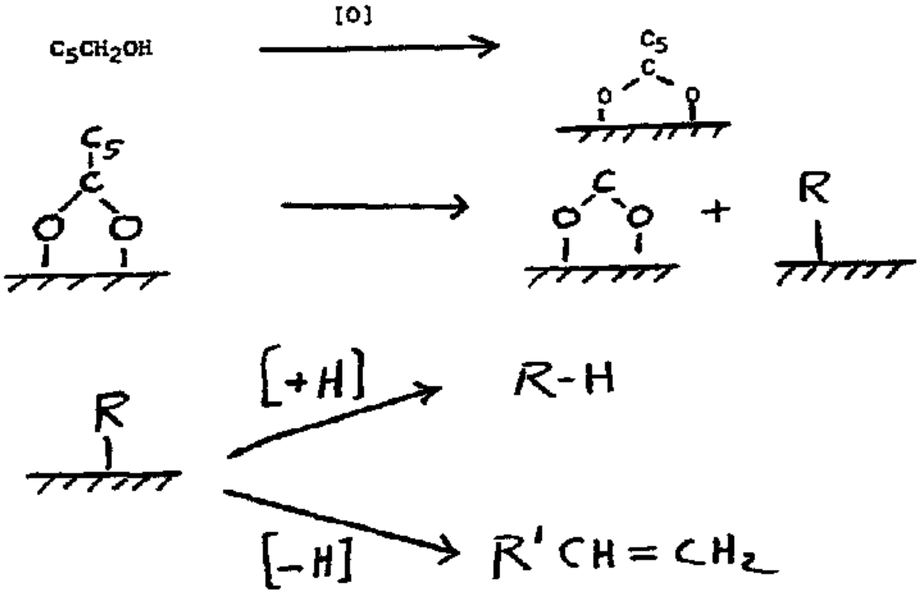


Figure III-57. Products (gas phase) from the conversion of syngas containing 1-hexanol[2-^{14}C] with a C-73 catalyst at 262°C and 7 atm. in a CSTR.

conversion of labeled 1-pentanol by the CO_2 produced by water-gas shift precludes a quantitative estimate of the ratio of decarbonylation to chain initiation; however, both alcohols produce similar results.

The data from the conversion of 1-hexanol [2-^{14}C] has serious implications for the chain growth mechanism. The alcohol should react with surface oxygen either prior to or following decarbonylation; thus, for reaction prior to decarbonylation we have:



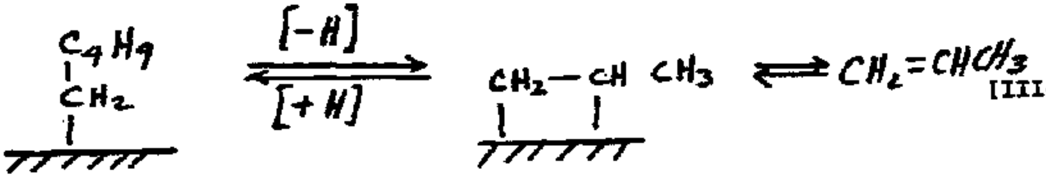
[III-32]

[III-33]

[III-34]

[III-35]

If preoxidation occurs to for the structure shown in equation III-32, or a similar structure, that decarbonylates to produce a C_5 alkyl species, then it appears that a similar alkyl group cannot be an intermediate in producing a significant fraction of the Fischer-Tropsch products. In the Fischer-Tropsch synthesis, 1 and 2-pentenes account for <u>ca</u>. 75% of the normal C_5 products. A chain growth mechanism that produces the C_5 species in equation III-32 could not then produce the necessary alkenes according to the following equation:



[III-36]

If the above reaction did occur and followed a selectivity similar to the normal Fischer-Tropsch synthesis, <u>ca</u>. 75% of the ^{14}C in the normal C_5 products should have been present in the pentenes. The radiochromatogram in figure III-58 clearly shows that this is not true. Rather, it appears that the n-pentane contains <u>ca</u>. 75% of the total ^{14}C present in the normal C_5 products. If this is the decarbonylation mechanism, then the half-hydrogenated state equilibration does not occur.

	G.C Ratio	P.C. Ratio
n–Pentane / I–Pentene	0.27	2.6

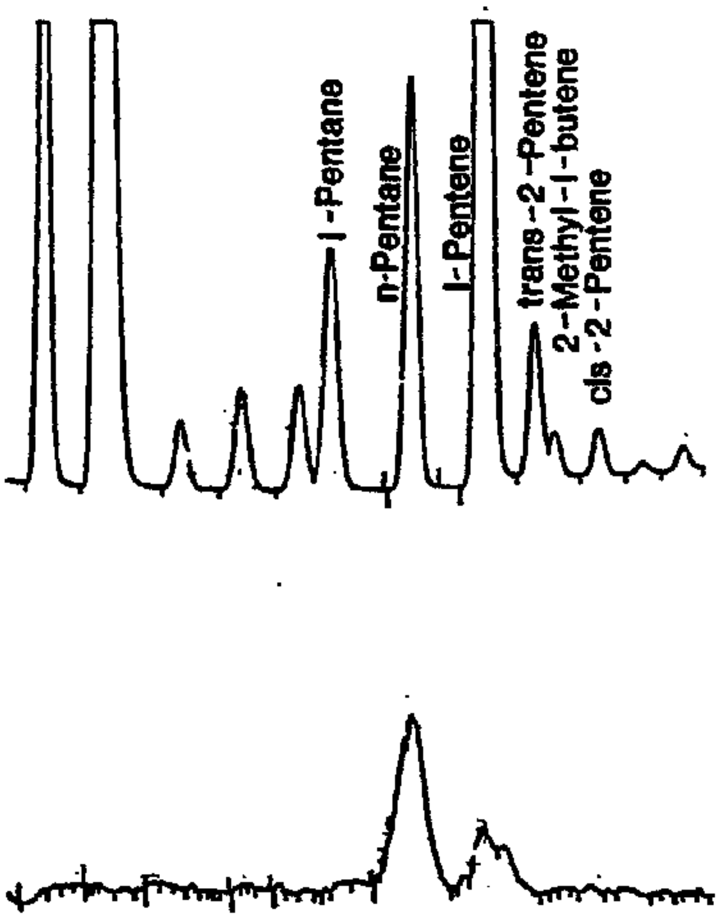
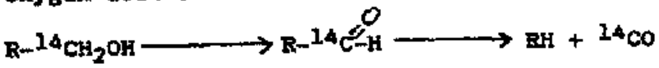


Figure III-58. Gas chromatogram (upper curve) and radiochromatogram (bottom curve) for the gaseous products when 1-hexanol[2-^{14}C] was added to the synthesis gas feed to a C-73 catalyst (CSTR, 252°C, 7 atm.).

Oxygen addition could also occur after the decarbonylation; e.g.



$$R\text{-}^{14}CH_2OH \longrightarrow R\text{-}^{14}\overset{O}{\overset{\|}{C}}\text{-}H \longrightarrow RH + {}^{14}CO \qquad [III\text{-}37]$$

However, ^{14}CO was present in much lower concentration $^{14}CO_2$. Thus, reaction III-37 is not responsible for the major fraction of the decarbonylation or the ^{14}CO produced by reaction III-37 is oxidized to $^{14}CO_2$ prior to desorption. For this latter event to occur, the CO produced by decarbonylation must be uniquely different from the CO adsorbed from the synthesis gas; if this is true then decarbonylation occurs on unique sites apart from the normal Fischer-Tropsch synthesis sites.

Another possibility is the following:

$$R^{14}CH_2OH \xrightarrow{H} RH + CH_2OH \xrightarrow{[O]} CO_2 \qquad [III\text{-}38]$$

This reaction is not considered to be likely since hydrogenolysis of the C-C bond as shown in III-38 would require the very unique reaction shown; otherwise, $^{14}CH_3OH$ would also be formed. Thus, a sequence involving reactions III-32 through III-35 is considered most likely.

1-Pentanol [1-^{14}C] in syngas was also converted with the ThO_2-Fe catalyst at 7 atm and 260°C in the fixed bed reactor. A hot spot developed during this reaction so that the results with the fixed-bed reaction are not directly comparable to those from the CSTR. Even so, they are of interest because most of the previous investigators used this type of reactor. The slope of the line defined by the log activity of the liquid products versus the carbon number (figure III-59) is much smaller than was obtained with the CSTR. For the alkene fraction the value is -0.05, a value not much different than 0.0 as expected for chain initiation by the alcohol. The slope for the higher carbon number alkane fraction is slightly higher (-0.8) and, while it does indicate some accumulation of the C_{18} - C_{22} alkanes in the catalyst pores, it is considerably smaller than for the alkanes produced when this alcohol was added to the feed to the CSTR. The difference in the activity in the alkene fraction obtained from these two reactors is shown in figure III-60; here the slope of the line defined by the CSTR data is -0.22 compared to the -0.05 for the fixed bed reactor. Similarly, the slope of the line defined by the alkane data from the fixed-bed reactor is -0.08 compared to the value of -0.13; it is likely that this latter value should be even more negative.

1-Decanol was also added to the syngas feed to the CSTR with C-73 catalyst at 260°C and 7 atmospheres. Here the alkene data fit the by now familiar pattern of a decrease in activity with increasing carbon number (figure III-61). In this case the slope was -0.28, a greater deviation from the value of zero than the other two alcohols showed with the C-73 catalyst. Extrapolating the straight line to carbon number 10 gives a value of 4.28 for the log CPM/ mole; this is about 12% of the activity of the alcohol charged. Thus, about 10-15% of the added alcohols was incorporated to produce hydrocarbons.

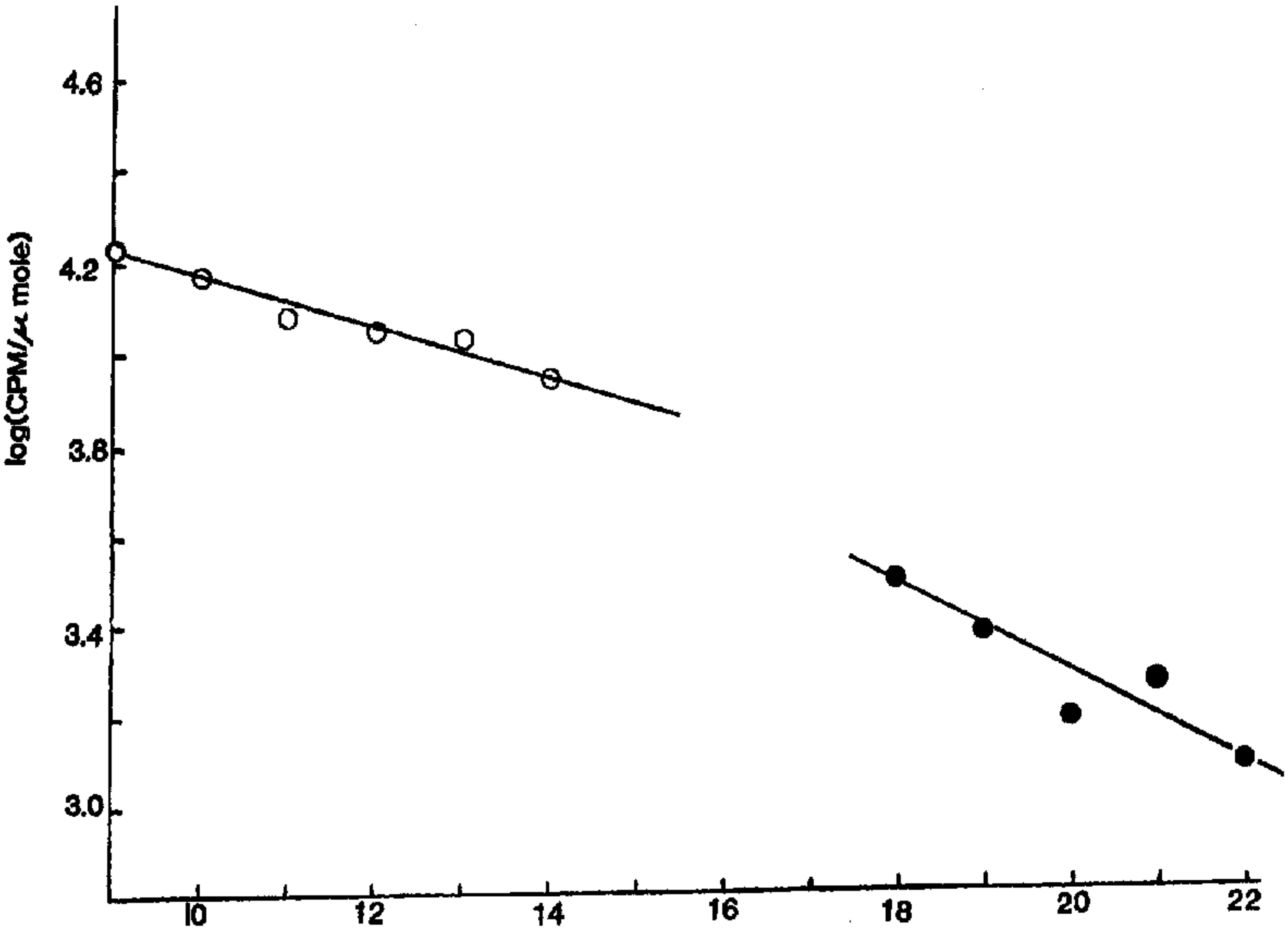
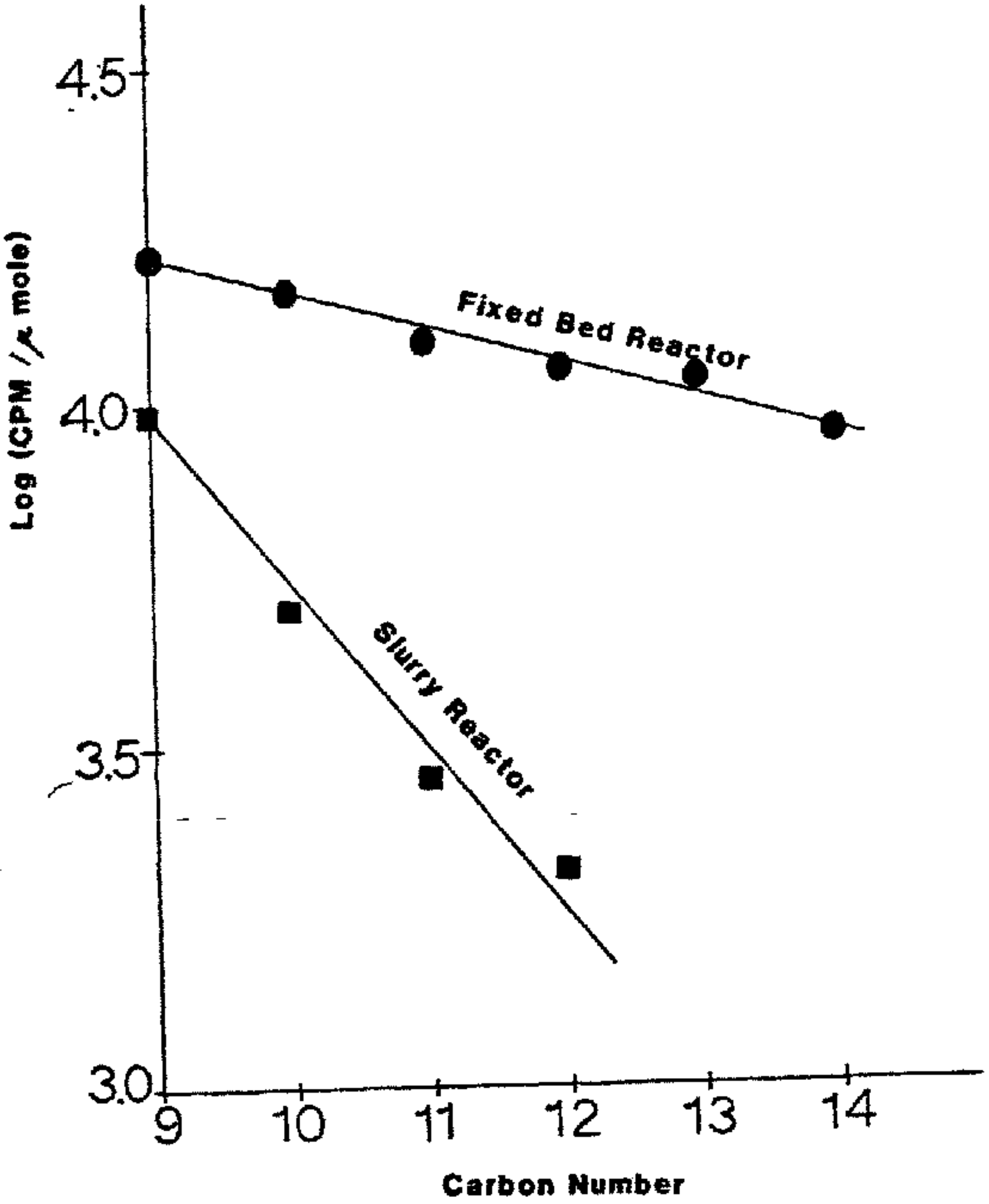


Figure III-59. Radioactivity in liquid product alkane (●) and alkene (○) fractions by liquid chromatographic separation of the products from syngas containing ^{14}C labeled 1-pentanol with a 6% ThO_2-Fe catalyst in a fixed-bed reactor at 260°C and 7 atm.

Figure III-60. Comparison of the activity in the alkene fraction from the Fischer-Tropsch synthesis when ^{14}C labeled 1-pentanol was added to a fixed bed or CST reactor (7 atm., 260°C).



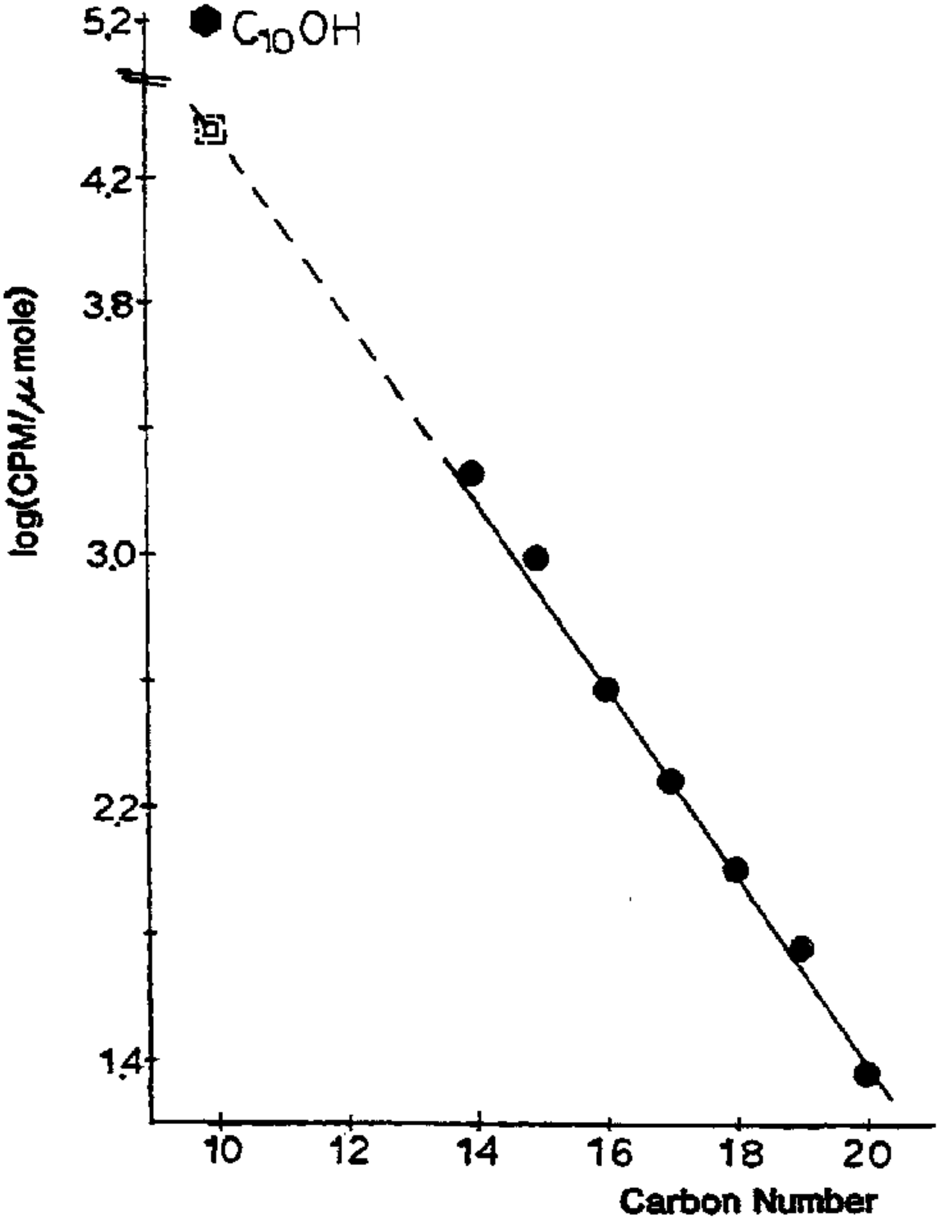


Figure III-61. ^{14}C activity of the alkane products versus carbon number when ^{14}C labeled 1-decanol was added to the feed to a C-73 catalyst (CSTR, 262°C, 7 atm.).

Ethanol [1-^{14}C] was added to the synthesis gas feed to Fe-SiO_2 catalyst in a CSTR maintained at 260°C and 7 atmospheres. This alcohol was incorporated (figure III-62) but again the accumulation of unlabeled hydrocarbons during the preceding period of operation with unlabeled synthesis gas diluted the alkanes so that the slope in figure III-62 was -0.20. Similar results were obtained using the C-73 and ThO_2-Fe catalysts with a synthesis gas containing labeled ethanol and a CSTR produced similar results.

However, when atmospheric pressure conditions were utilized with ethanol [1-^{14}C] containing syngas to a fixed bed reactor at 260°C the result differed from those of the CSTR runs. As shown in figure III-63, the slope of the line defined for the alkane data is -0.04, nearly the zero value expected for initiation of chain growth by the added ethanol. Thus, the atmospheric pressure data for higher alkanes with the average hydrocarbon data reported by Emmett and summarized in the Introduction.

The activity of the alkane fraction as a function of carbon number is summarized in figure III-64 for C-73 and Fe-SiO_2 catalysts. The slopes for C_2, C_5 and C_{10} alcohol and alkene feed to the C-73 catalyst are shown in figure III-65. Since accumulation impacts these data, and this was not appreciated nor controlled accurately during the course of this study, they serve to emphasize the importance of accumulation from earlier runs upon the results produced by a processing change. These data serve to show the severe analytical requirements for mass balances if a CSTR is to be used in Fischer-Tropsch synthesis studies where process variables are charged frequently (i.e. every <u>two</u> weeks or so).

III-J. Comparison of Initiation by Alcohol and Alkene

The log CPM/μ-mole versus carbon number for the alkane products data are shown in figure III-66. It is clear that the alcohol was incorporated to a much greater extent than the pentene. Comparison of the activity of the pentene added and the value obtained by extrapolating to the activity of the C_5 alkane produced during the addition indicates that <u>ca</u>. 3% of the pentene initiated chain growth while a similar calculation shows that <u>ca</u>. 50% of the added pentanol initiated chain growth.

A similar trend is observed for the comparison of the initiation by ethanol and ethene. As indicated in the figure III-67, 60 to 80 times more ethanol was incorporated than ethene (different batches of labeled ethanol was used for the two runs).

The situation with C_{10} appears to be quite different from the situation with the C_2 and C_5 compounds. As shown in figure III-68, the alkene is, in carbon range shown, incorporated to a greater extent than decanol; following the extrapolation to the carbon number ten shows that about 10% decanol incorporation and about 20% 1-decane incorporation.

The relative activity expressed as CPM/μ-mole for the alkane produced from the alcohol divided by that from the alkene is shown for a range of carbon numbers in figures III-69 and III-70. In figure III-69, data are shown for duplicate separations of the products formed from ethanol or ethene containing syngas with the C-73 catalyst. Considering the experimental procedures the agreement is excellent. It clearly shows that, for these

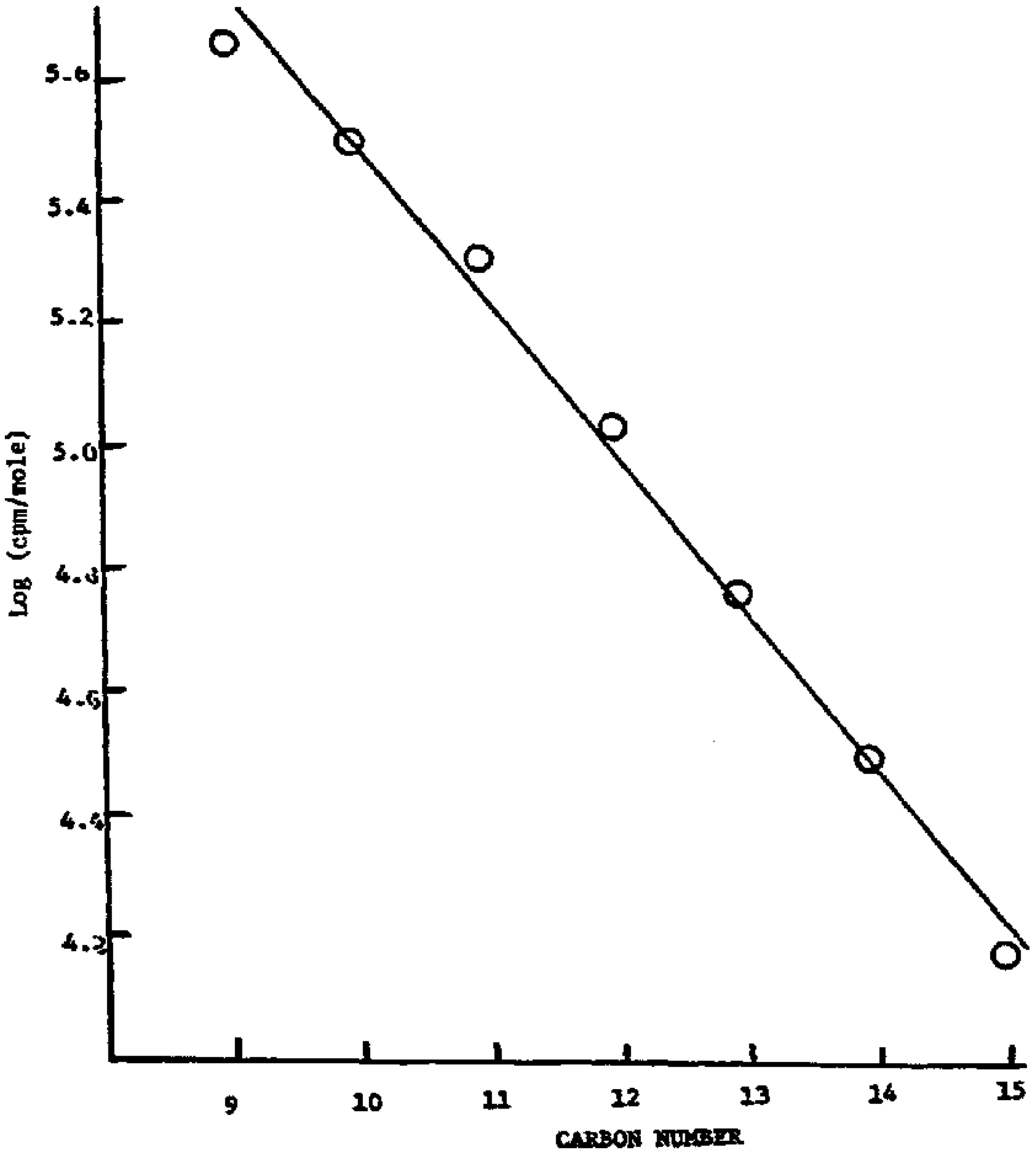


Figure III-62. Log (counts per minute/mole hydrocarbon) of the n-alkane fraction separated from the products produced from CO/H_2 with added C-14 labeled ethanol conversion over an $Fe-SiO_2$ catalyst at 260°C and 7 atmospheres pressure.

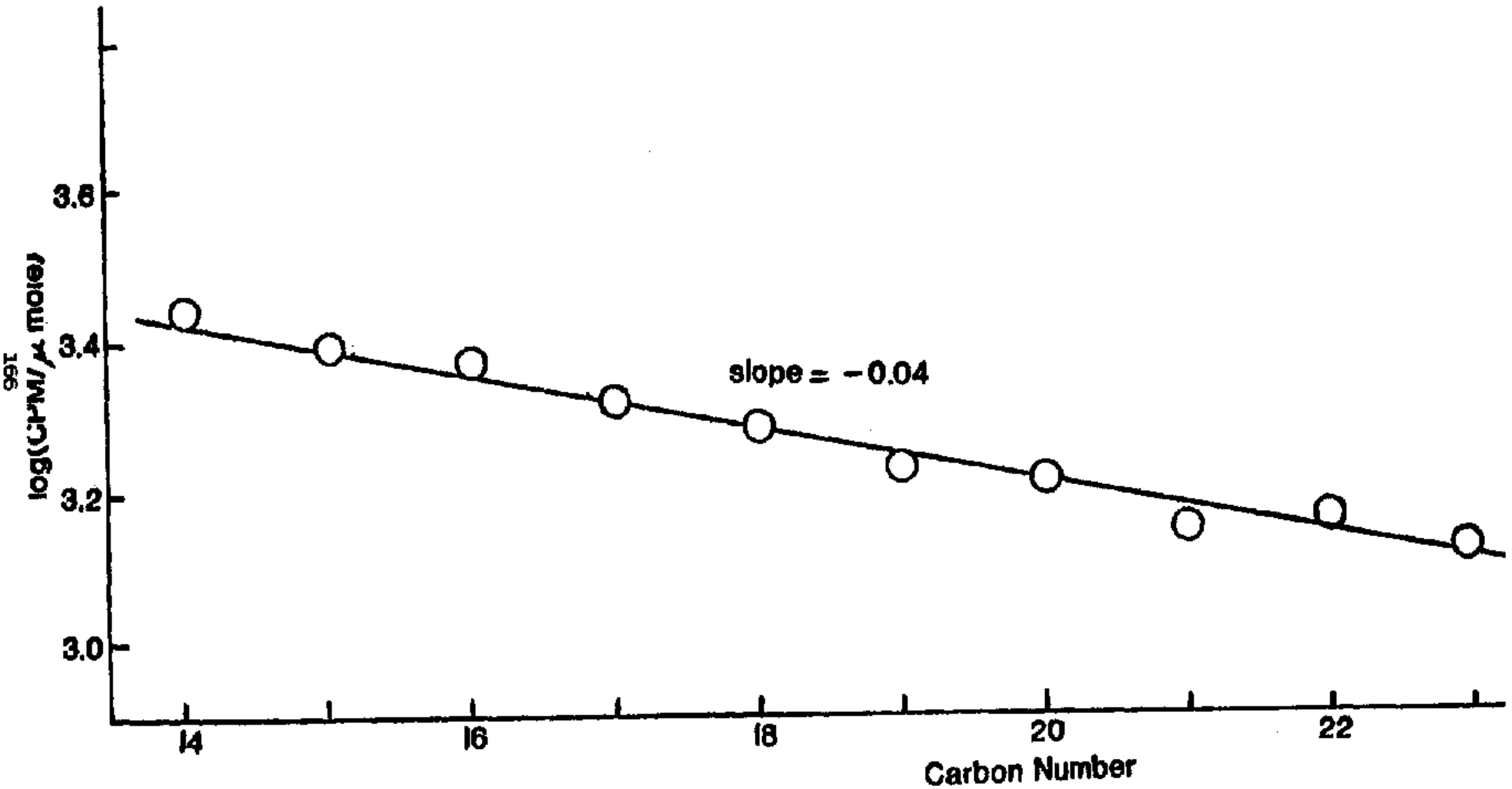


Figure III-63. ^{14}C activity versus carbon number for the alkanes produces when ^{14}C labeled ethanol was present in the syngas feed to a C-73 catalyst (fixed-bed reactor, 260°C, 1 atm.).

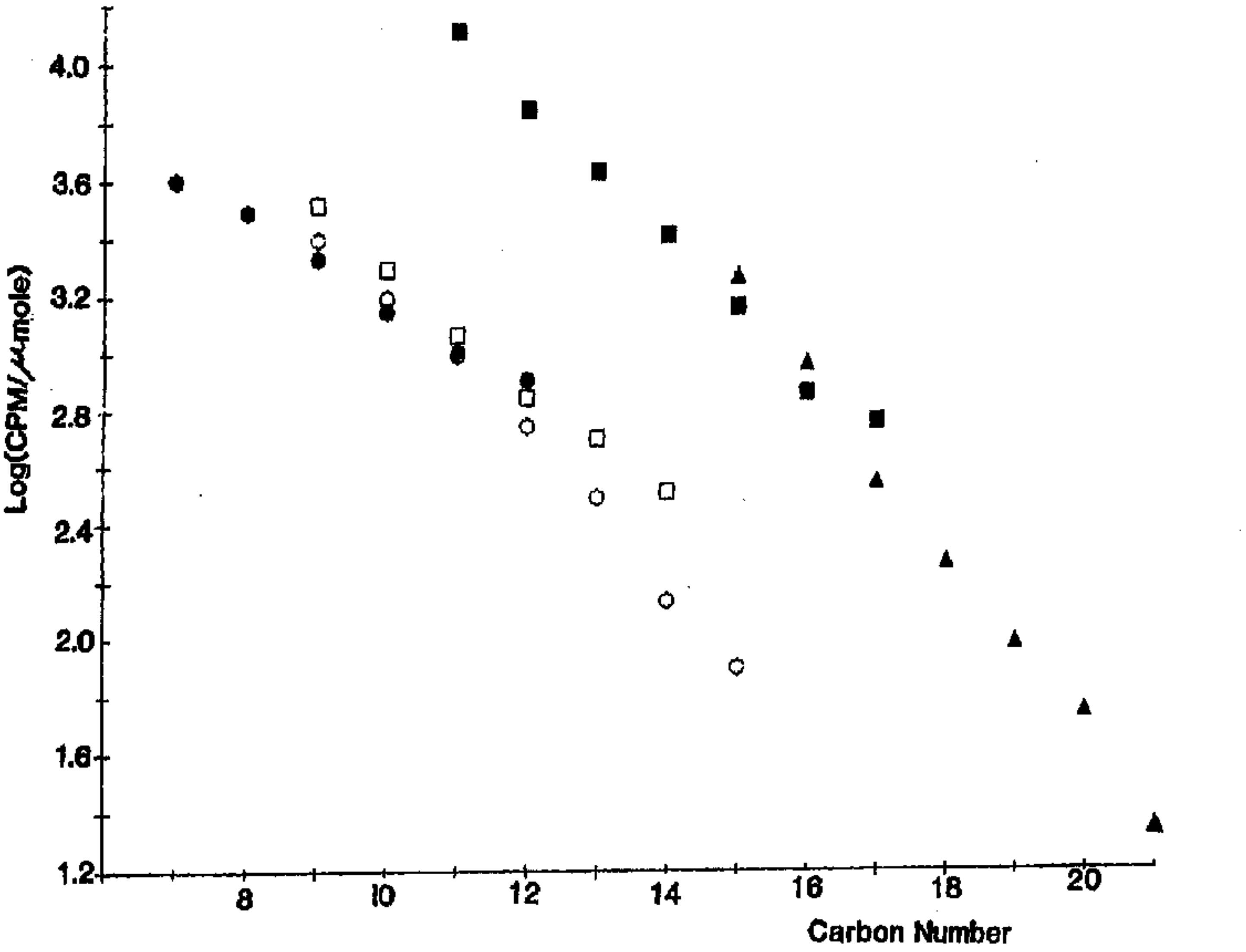


Figure III-64. ^{14}C activity in the alkane fraction of the Fischer-Tropsch synthesis for: (■) labeled ethanol and C-73; (●) labeled 1-pentanol with C-73; (▲) labeled 1-decanol with C-73; (○) labeled 1-pentanol and 10% Fe-SiO$_2$; and (□) labeled ethanol and 10% Fe-SiO$_2$ (CSTR, 252°C, 7 atm.).

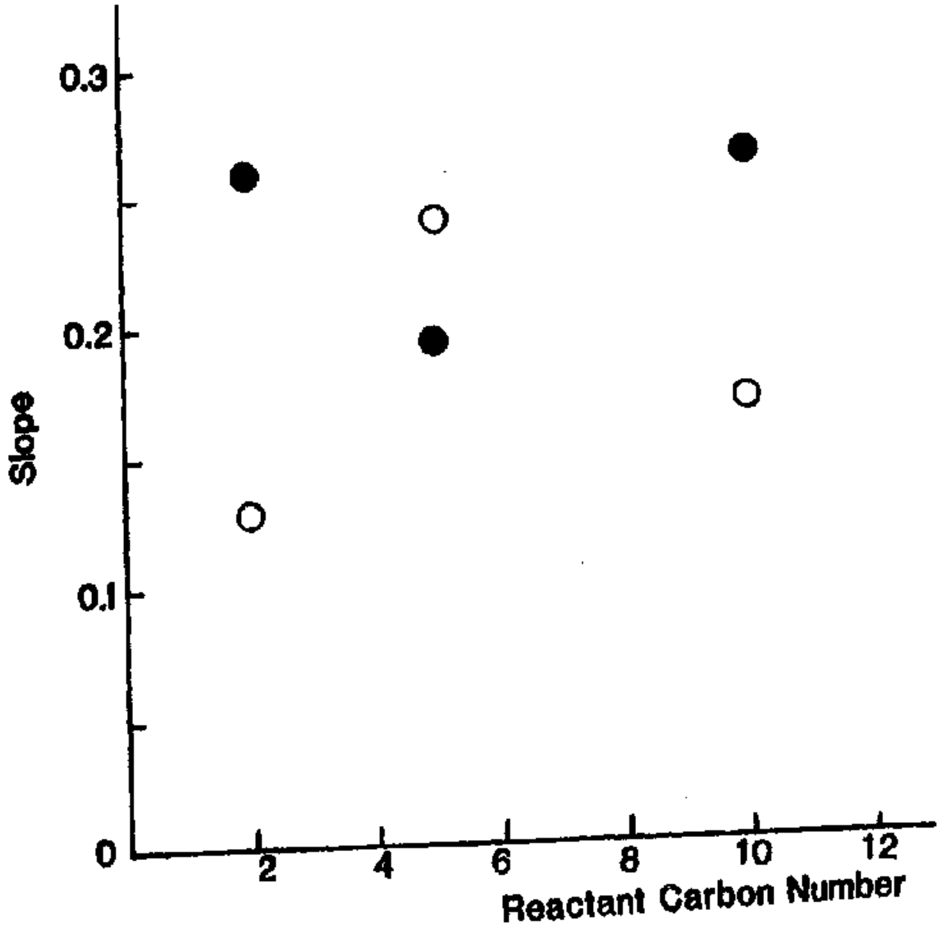


Figure III-65. Slope of the line for log (CPM/ mole) versus carbon number for the alkane fractions produced when 1-alkanol (●) or 1-alkene (○) was added to the syngas feed to a C-73 catalyst using a CSTR, 262°C and 7 atmosphere conditions.

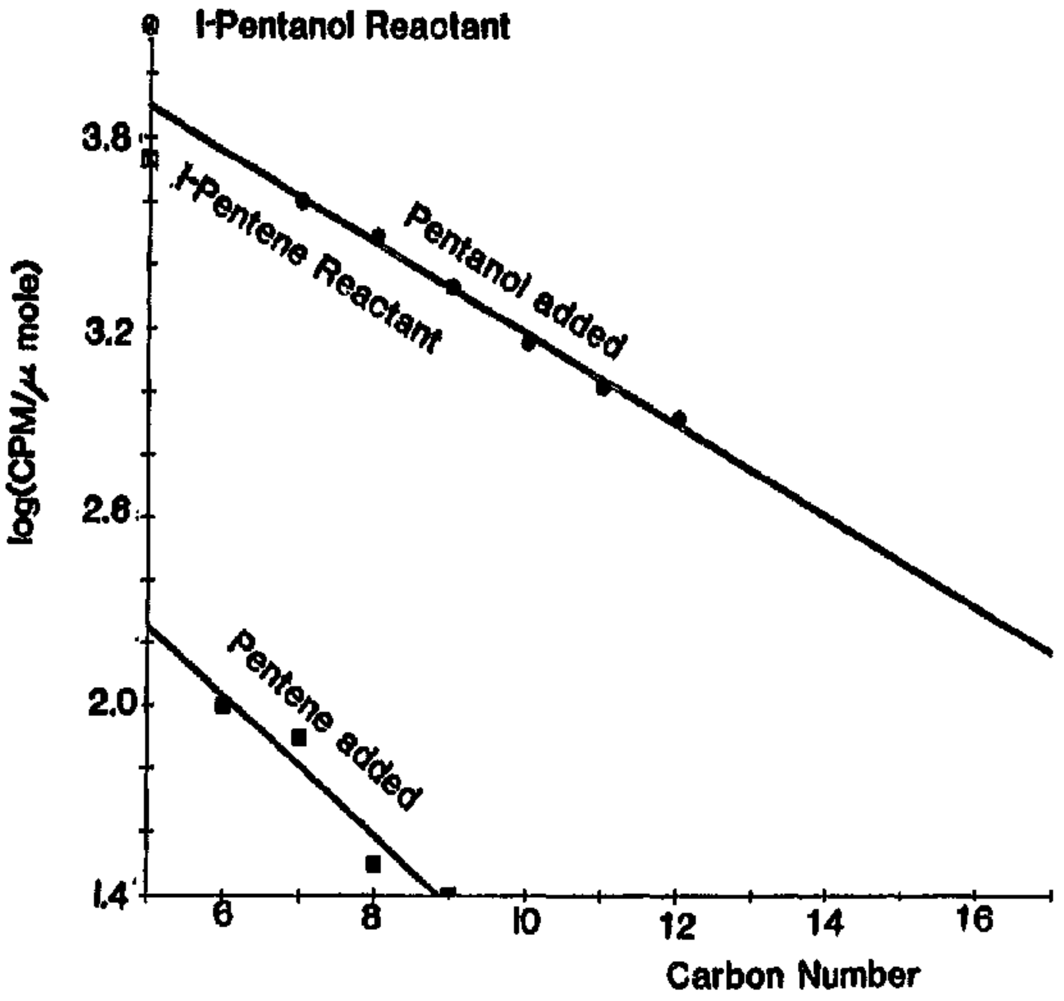


Figure III-66. The ^{14}C activity in the alkane products formed when 1-pentanol (●) or 2-pentene (■) was added to the syngas feed to a C-73 catalyst (CSTR, 262°C, 7 atm.).

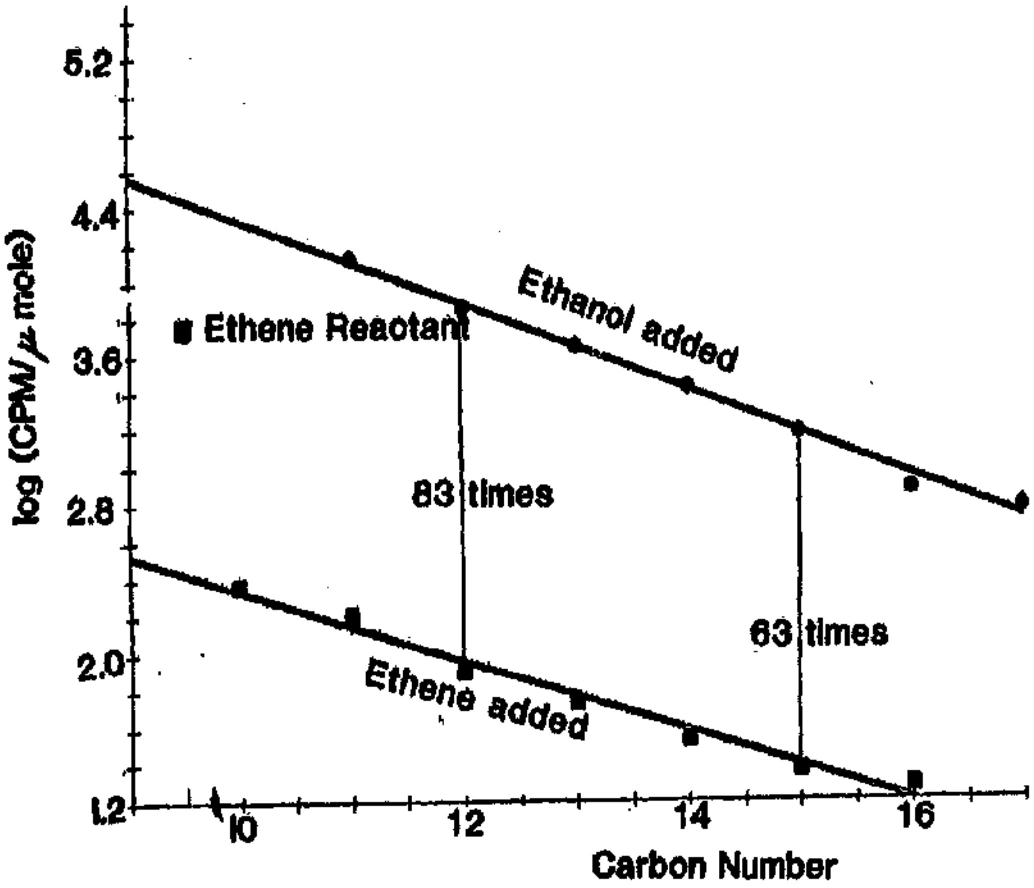


Figure III-67. The ^{14}C activity in the alkane products formed when ethanol (●) or ethene (■) was added to the syngas feed to a C-73 catalyst (CSTR, 262°C, 7 atm.).

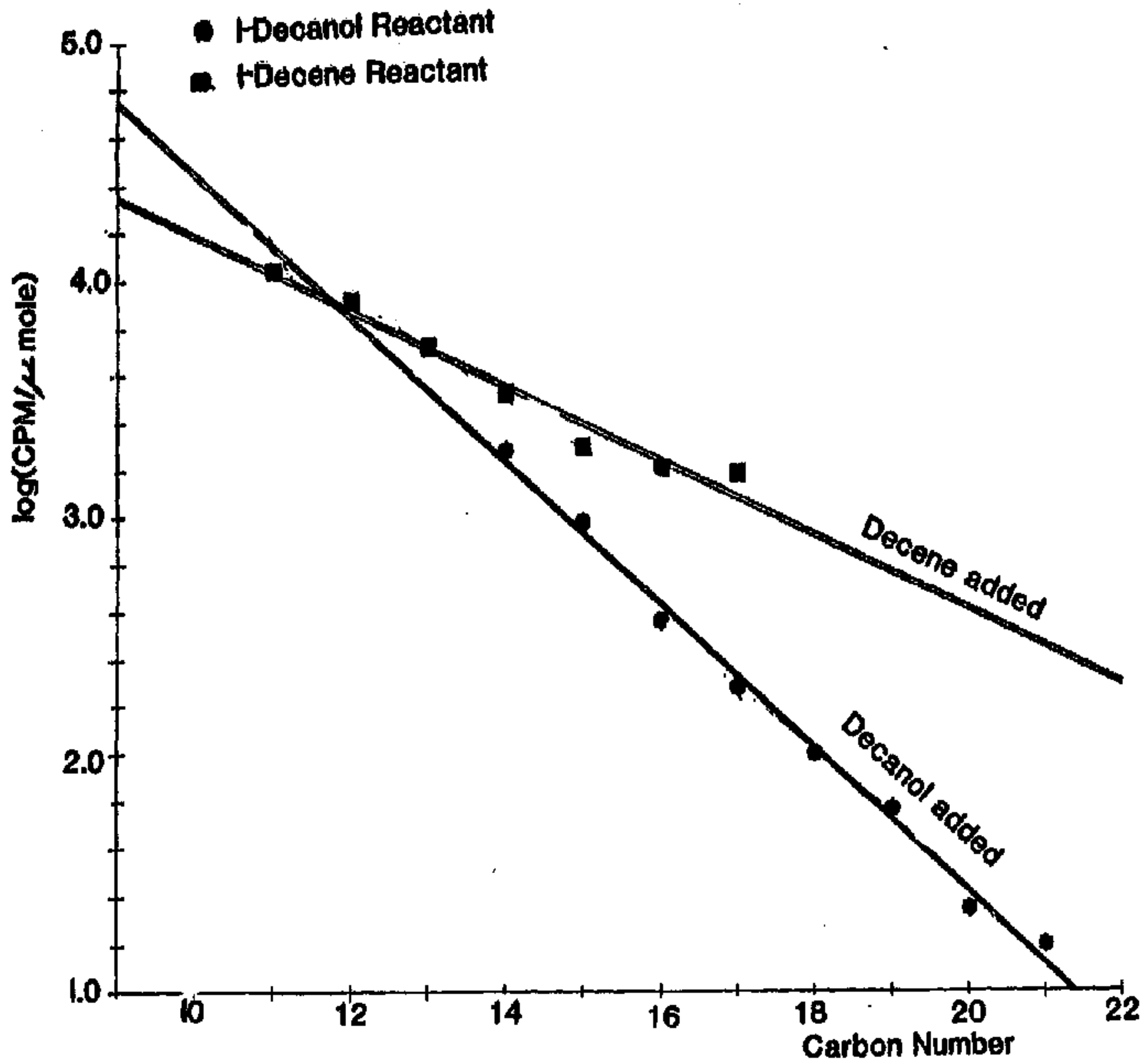


Figure III-68. The ^{14}C activity in the alkane products formed when 1-decanol (●) or 1-decene (■) was added to the syngas feed to a C-73 catalyst (CSTR, 262°C, 7 atm.).

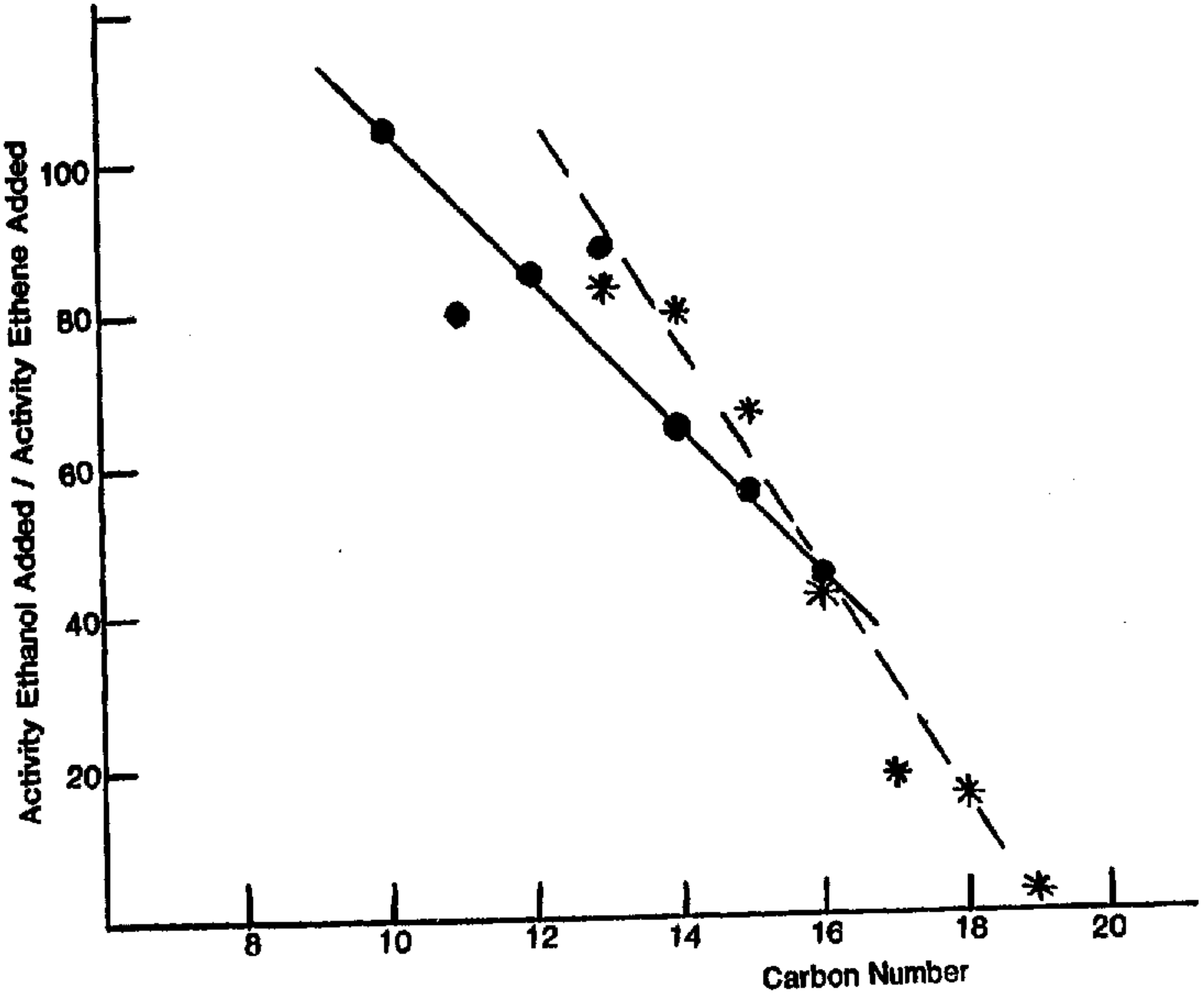


Figure III-69. Ratio of the activity in the alkane produced when labeled ethanol was added to the syngas versus carbon number (C-73, CSTR, 262°C, 7 atm.).

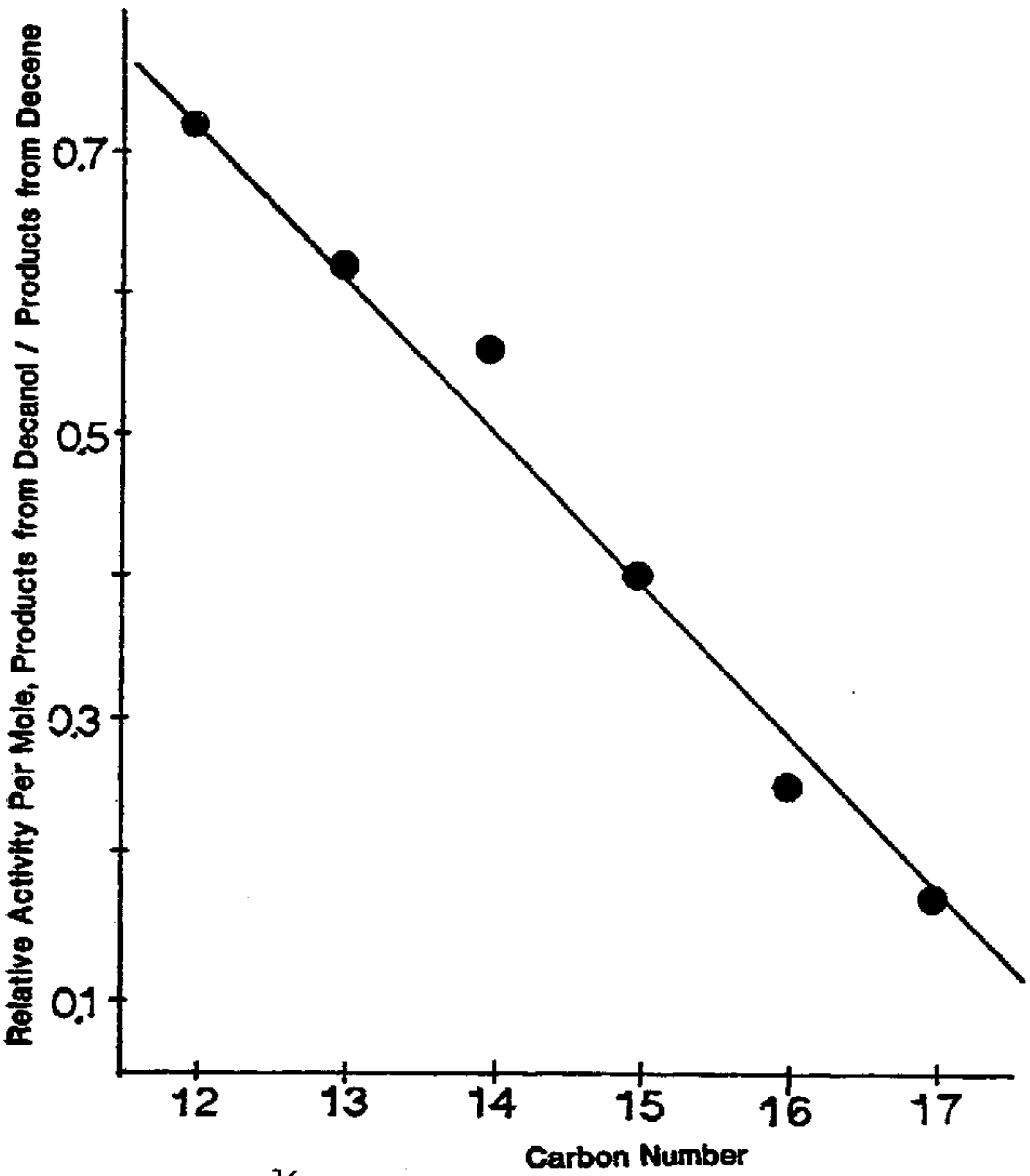


Figure III-70. Relative ^{14}C activity per mole (CPM/mole in alkanes when 1-decanol was added divided by CPM/mole in alkanes when 1-decene was added) versus carbon number (CSTR, 262°C, 7 atm.).

intermediate carbon number alkanes, the alcohol is a much more effective initiator. For the decanol and decene results, a similar trend is observed (figure III-70) but the ratio is now in the range of 0.1 to 0.7 rather than the range observed with the C_2 compounds, 10 to 100. Thus, it appears that the distinction between initiation by alcohol and alkene decreases with increasing carbon number and becomes essentially the same for C_{10}.

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