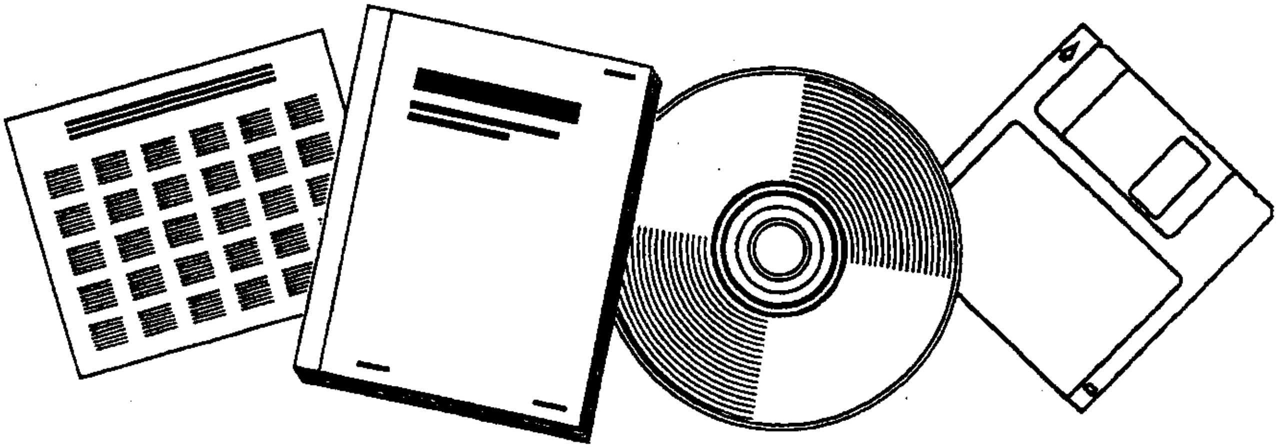
DE87013807 80015-7

FISCHER-TROPSCH SLURRY PHASE PROCESS VARIATIONS: QUARTERLY REPORT FOR PERIOD APRIL 1, 1987 TO JUNE 30, 1987

MASSACHUSETTS INST. OF TECH., CAMBRIDGE

1987



U.S. DEPARTMENT OF COMMERCE
National Technical Information Service

Fischer-Tropsch Slurry Phase
Process Variations

DOE/PC/80015--7

DE87 013807

Quarterly Report for Period
April 1, 1987 to June 30, 1987

Report No.: DOE/PC80015-7

Contract No.: DE-AC22-85PC80015

Submitted by:

Charles N. Satterfield

Summary

Our studies of the effects of adding various selected olefins during Fischer-Tropsch synthesis have now been summarized in the form of a paper for publication, attached. The principal observations and conclusions are:

In studies with a reduced fused magnetite catalyst at 248°C, and 0.78 to 1.48 MPa, reactions of the added species were much more significant at high synthesis conversions where the relatively lower partial pressure of CO allowed competitive adsorption effects with CO to become more important. Ethanol decreased hydrogenation capabilities of the catalyst as reflected in lower CH_4 formation and higher olefin-paraffin ratio. Excluding ethylene, which is unusually reactive, the reactivity of an 1-olefin increased with molecular weight, but almost exclusively to form the corresponding paraffin or β-olefin. Incorporation of olefins into growing chains was relatively small.

Reactions of Ethanol and Selected 1-Olefins Added During the Fischer-Tropsch Synthesis

Abstract

In studies with a reduced fused magnetite catalyst at 248°C, and 0.78 to 1.48 MPa, reactions of the added species were much more significant at high synthesis conversions where the relatively lower partial pressure of CO allowed competitive adsorption effects with CO to become more important. Ethanol decreased hydrogenation capabilities of the catalyst as reflected in lower CH_4 formation and higher olefin-paraffin ratio. Excluding ethylene, which is unusually reactive, the reactivity of an 1-olefin increased with molecular weight, but almost exclusively to form the corresponding paraffin or β-olefin. Incorporation of olefins into growing chains was relatively small.

Introduction

In the Fischer-Tropsch synthesis, in addition to paraffins, 1-olefins and 1-alcohols are significant primary products. Once formed, these latter can undergo secondary reactions such as hydrogenation, isomerization, and possibly incorporation into growing chains. The objective of this work was to study such secondary reactions of selected primary products by adding the compound of interest to the synthesis gas feedstream or directly to the reactor under normal Fischer-Tropsch synthesis conditions. The compounds studied were ethanol, ethylene, 1-butene, 1-hexene, 1-decene and 1-eicosene ($C_{20}H_{40}$). In the primary synthesis ethanol is the dominant alcohol and C_2 species appear to be unusually reactive. The other olefins were studied to see if any regularities would be found with increasing molecular weight of this homologous series.

Experimental Apparatus and Materials

The experiments were conducted using a 1-liter, well-mixed slurry phase reactor. The experimental apparatus and materials were as described previously (1,2). The one exception was the addition to the system of a liquid pump to introduce a selected compound of interest. For each run, about 70 grams of crushed catalyst (270-325 mesh) were reduced and then slurried with about 420 grams of purified octacosane. The behaviour of the same fused magnetite catalyst under a variety of conditions has also been described (3,4). The compounds used in this study are listed in Table 1.

Experimental Procedure

In general, experiments with and without each compound listed in Table 1 were conducted at 248°C, pressures in the range of 0.78 to 1.5 MPa, high and low CO conversions, and with high and low concentrations of the additive in the feed. CO conversion was varied by changing the flow rate of synthesis gas to the reactor.

Three lengthy sets of runs were made. For each run, at least 40 hours were first allowed to elapse after the freshly reduced catalyst was brought on-stream to insure that steady state activity had been achieved. A material balance was then run without additive addition for about 6 hours to establish a base case. The additive was then introduced continuously for some 4 to 10 hours after which steady state was essentially achieved and a material balance was then obtained over a 6-7 hour period. The same additive at a different concentration or another additive was then introduced and the same procedure repeated. Each run extended over several hundred hours and from time to time the base case was re-run to insure that no significant change in catalyst activity or selectivity had occurred. To avoid any systematic bias the order of experiments was randomized both with respect to reactor conditions and the nature of the additive.

Ethylene and 1-butene were introduced by using tanks of premixed gases. Ethanol, 1-hexene and 1-decene were introduced as liquids by a liquid pump. For 1-eicosene the reactor was taken off stream after 50 hours of synthesis and a known weight of 1-eicosene was directly injected into the reactor under inert gas pressure after it was melted. The reactor was then put back on stream and a sample of the reactor wax was taken after 8 hours of resumed synthesis.

The base case experiments previous to addition of ethylene or 1-butene were conducted at each of two pressures, 0.78 and

1.48 MPa. The subsequent experiments were done at slightly higher total pressure in the reactor to maintain constant partial pressure of CO in the presence of the increased partial pressure of the feed additive. This increase in pressure amounted to a maximum of about 100 kPa for the highest concentration of ethylene or about 40 kPa for the highest concentration of 1-butene. Because of physical limitations of the pump, the highest operating pressure of the experiments when a liquid was added (C_6 and C_{10}) was 0.92 MPa. The operating pressure for the 1-eicosene experiment was also 0.92 MPa. For direct comparison each additive was studied at least in part at the same set of synthesis conditions (248°C, 0.92 MPa, high CO conversion).

RESULTS AND DISCUSSION

The conditions for all of the experiments are summarized in Table 2 together with the resulting CO and H_2 conversions and the resulting partial pressures of the feed additive in the exit gas of the reactor. In all cases the addition of the selected olefin or ethanol significantly increased the partial pressure of the additive in the reactor over that which existed during normal Fischer-Tropsch synthesis.

Results - Ethanol

The conversion of the ethanol in the feed was calculated by first subtracting the flowrate of ethanol leaving the reactor for the experiments with no feed addition (base case) from the flowrate of ethanol leaving the reactor for the feed addition experiments conducted at the same conditions. Together with the value of the ethanol flowrate fed to the reactor, the conversion and rate of consumption of the ethanol in the feed were calculated. At high CO conversion, the averaged conversion of ethanol in the feed was about 30%, while for the single experiment conducted at low CO conversion, the conversion of the ethanol in the feed was less than 1%.

The addition of ethanol to the feed did not significantly affect the CO or H_2 conversions at low CO conversions (40-42%) (Table 2). At high CO conversions (88-93%), the ethanol addition resulted in a slight decrease in H_2 conversion but had no significant effect on CO conversion.

Shown in Table 3 are the pertinent selectivity results from the experiments with ethanol. At both high and low CO conversions, the increased partial pressure of ethanol in the reactor resulted in a significant decrease in methane selectivity, and an increase in the olefin/paraffin and α-olefin/β-olefin ratios. The latter two ratios were more affected by ethanol at high CO converions. The ethylene concentration in the exit gas significantly increased upon ethanol addition, especially at high CO conversions. However, that of ethane decreased by approximately an equal amount, as reflected by the essentially constant overall selectivity to form ethylene plus ethane.

The selectivity to form C_3 hydrocarbons (propane and propylene) remained essentially constant, but there was an increased selectivity to form ethanal (acetaldehyde), C_3 oxygenates, (propanol and propanone) and ethyl acetate. The last compound was positively identified (Cambridge Analytical

Associates, Inc.) using g.c. mass spectrometer analysis and further confirmed in our laboratories using ethyl acetate as a spike in the g.c. samples. The C_3 oxygenates could not be accurately separated quantitatively into propanol and propanone, but careful analysis of the samples containing the C_3 oxygenates revealed that an increase in the overall C_3 oxygenate selectivity was due to an increase in propanone. By a material balance most of the ethanol disappearance could be accounted for by appearance of acetaldehyde, C_3 oxygenates and ethyl acetate, i.e., the increase in ethylene concentration could be attributed to less secondary hydrogenation of ethylene rather than ethanol dehydration.

The effect of ethanol addition at a high CO conversion on the C_1-C_7 product distribution is shown in Figure 1. This is normalized excluding the C_2 fraction. The methane selectivity dropped but the chain growth probability as characterized by α was not significantly affected. Ethanol addition had no significant effect on the amount of CO_2 formed per mol of CO consumed, i.e., it did not affect the water gas shift. Because of the normalization procedure, the amounts of C_1 and C_3-C_7 must add up to unity. The results presented in Fig. 1 do not mean that more C_3-C_7 is produced with higher ethanol addition.

Discussion - Ethanol

Added ethanol did not significantly affect the conversion of CO, suggesting either weak adsorption of the ethanol relative to CO or, less likely, adsorption of the ethanol on sites other than those active for CO adsorption. A similar lack of synthesis inhibition by ethanol was also observed by Kokes et al. (5). In that study, synthesis gas (H_2/CO = 1) containing C^{14} labelled ethanol (1.5 vol%) was passed over a reduced singly-promoted iron catalyst (0.64% Al_2O_3 and 2.00% ZrO_2) at 239°C and 1 atm, and over a reduced doubly-promoted iron catalyst (4.6% MgO, 0.6% K_2O, 0.6% SiO_2, and 0.6% Cr_2O_3) at 241-275°C and 1-21.5 atm. For both catalysts the ethanol addition did not retard the synthesis.

In a similar study by Kummer et al. (6), when synthesis gas (H_2/CO = 1) was passed over a reduced singly promoted iron catalyst (1.55% Al_2O_3 and 0.58% ZrO_2) at about 230°C and 1 atm, the addition of C^{14} labelled ethanol (1.6 vol%) reportedly retarded the synthesis. However, catalytic activity was characterized indirectly by gas contraction, rather than CO conversion. The constant CO conversion and decreased H_2 conversion upon ethanol addition observed here, of course corresponds to decreased overall contraction.

The added ethanol decreased the hydrogenating characteristics of the catalyst, as reflected in the decrease in methane selectivity and the increase in C_2-C_4 olefin/paraffin ratios. The latter also suggests that the ethanol is competitively adsorbing with the α-olefins for active sites, thus inhibiting the secondary reactions of the α-olefins. This is supported by the observation that the α-olefin/β-olefin ratios also increased with increasing ethanol partial pressure. Kummer et al. (6) also noted this decrease in the hydrogenating activity of the catalyst with added ethanol as evidenced by the increase in the C_2, C_3, and C_4 olefin/paraffin ratios.

The decrease in methane selectivity cannot be attributed to the reaction of adsorbed ethanol with adsorbed methane precursors such as CH_3*. Such a reaction should result in a significantly increased selectivity to form C_3 species, but this was not found. The increase in the C_2 olefin/paraffin ratio is not the result of an increased formation of ethylene caused by ethanol dehydration, since then the total C_2 hydrocarbon selectivity, ethylene plus ethane, would increase with added ethanol. Once again, this was not observed.

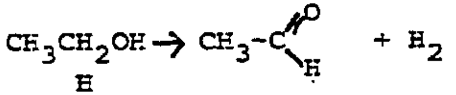
All of the above effects were more dominant at the higher CO conversions. At the correspondingly lower CO partial pressures, more sites are available for the ethanol to adsorb and interact with the ongoing synthesis.

Ethanol did not significantly incorporate into growing hydrocarbon chains to form higher hydrocarbons, as evidenced by the lack of increase in the C_3 hydrocarbon (i.e., propane plus propylene) selectivity with added ethanol. In contrast, in the study of Kummer et al. (6) at atmospheric pressure about 35% of the labelled ethanol added was incorporated and the resulting hydrocarbon products (up to C_{10}) had approximately a constant radioactivity per mole, suggesting that ethanol could act as a chain initiator. It was further shown that the chain initiation occurred preferentially at the methylene carbon atom.

Kokes et al. (5) extended the work of Kummer et al. by C^{14} tracer experiments with a doubly-promoted catalyst at varying pressure and temperatures (239-275°C). The percent incorporation of the ethanol was not a function of temperature or contraction, but fell from 18 to 7 to 2.2% as the pressure was increased from 1 to 7.5 to 21 atm. They also concluded by comparison to Kummer et al.'s results that less incorporation occurred over a doubly-promoted catalyst (MgO, K_2O) than over a singly-promoted catalyst (ThO_2).

The lack of evidence for significant ethanol incorporation in this study is consistent with the conclusions of Kokes et al. since the experiments here were at relatively high pressures (0.92 MPa) over a triply-promoted catalyst (Al_2O_3, K_2O, CaO). However, if a small degree of incorporation did occur, it could not have been detected with the analytical techniques employed here.

The observed increase in selectivity to form both acetaldehyde and ethyl acetate with an increase in ethanol partial pressure are probably interrelated. The acetaldehyde is probably produced by dehydrogenation of the ethanol (Reaction 1) and the ethyl acetate by the subsequent reaction of the acetaldehyde with ethanol (Reaction 2).



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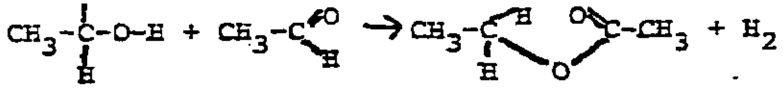


(2)

The observed increase in selectivity to form propanone (acetone) with an increase in ethanol partial pressure suggests that the ethanol is possibly reacting with surface methylene species by a reaction such as 2a.

$$CH_3CH_2OH + CH_2^* + H^* \rightarrow CH_3COCH_3 + H_2 \quad (2a)$$

The fact that propanone was formed in Reaction 2a instead of 1-propanol further suggests that the ethanol is bonded to the catalyst surface at the oxygenated carbon. The hydrogen produced via Reactions 1, 2 and 2a would account for less than 10% of the observed decrease in hydrogen conversion. This decrease thus reflected rather a decrease in the activity of the hydrogenation functionality of the catalyst.

Results - Olefins

Ethylene

The addition of ethylene did not significantly affect the CO conversion but H_2 conversion increased, especially at high CO conversions (Table 2).

The effect of the ethylene partial pressure in the reactor on the methane selectivity is shown in Figure 2 for all of the experiments. Methane selectivity decreased with increasing ethylene partial pressure at both high and low CO partial pressures. Increased ethylene partial pressure increased the C_3 and C_4 olefin/paraffin ratios (Figure 3). Although not shown, the α-olefin/β-olefin ratios also increased with ethylene partial pressure, but only slightly.

The effect of ethylene on the Fischer-Tropsch product distribution at 91-93% CO conversion is shown in Figure 4. The C_1-C_7 product distribution is normalized without the C_2 fraction. The decreased methane selectivity at high ethylene partial pressure is clearly evident, but there was no effect of ethylene concentration on α.

The conversion of the ethylene in the feed was calculated in the same manner as was the conversion of ethanol. Likewise, the rate of formation of a compound resulting from the reaction of ethylene was determined by subtracting the base case rate of formation of that compound from the rate of formation of that compound during the feed addition experiments. The assumption inherent in these calculations is that the ethylene did not significantly affect the normal Fischer-Tropsch synthesis, which seems reasonable.

At high CO conversions (86 to 94%) the conversion of the ethylene in the feed was between 56 and 86%, while at low CO conversions (27 to 29%) it was between 8 and 11%. At low CO conversions, essentially all of the ethylene in the feed that was consumed, formed ethane. At high CO conversions, between 70 and 80% of the ethylene consumed formed ethane. Presumably then between 20 and 30% of the consumed ethylene that reacted, or about 15% of the ethylene fed to the reactor, was incorporated into the growing hydrocarbon chains on the catalyst surface to form heavier hydrocarbon products. This is supported by Figure 5, which plots the selectivity to form C_3 hydrocarbons (i.e., propane and propylene) as a function of ethylene partial pressure in the reactor. Under otherwise similar conditions, with increasing ethylene partial pressure in the reactor there is an increase in the formation of heavier hydrocarbons. This effect is most pronounced at high CO conversions.

Some previous studies, although very fragmentary, showed effects in the same direction found here. Snel and Espinoza (7) working at 270°C and 2.0 MPa with iron-calcium catalyst containing about 3 atomic % C reported addition of 10 mole % ethylene to syngas ($H_2/CO = 0.5$) to depress methane formation, to increase formation of higher hydrocarbons, and to increase the olefin content of products formed. Molina et al. (8) working with a 10% Fe/Al_2O_3 catalyst at atmospheric pressure, 250°C, were primarily concerned with studying the effect of introduction of CO into a H_2-C_2H_4 mixture. However they likewise reported that the presence of C_2H_4 in a H_2/CO reaction mixture enhanced C_3 products and reduced methane formation.

With increasing ethylene partial pressure in the reactor there is a strong increase in the selectivity to form 1-propanol, as shown in Figure 6, although the concentrations are small relative to the total C_3 hydrocarbons. This does not appear to be dependent on the CO partial pressure. There was also an increasing selectivity to form 2-butanone. For example, for $P_{C_2H_4} = 5.1$ kPa, the ratio of 2-butanone production to CO consumption was 9.3×10^{-6}, while for $P_{C_2H_4} = 68$ kPa, the ratio was 6.3×10^{-4}.

<u>1-Butene</u>

The addition of 1-butene to the syngas feedstream did not significantly affect the CO or the H_2 conversions, methane selectivity, olefin/paraffin ratio or the α-olefin/β-olefin ratios. No significant changes in the C_3 hydrocarbon selectivity or in C_4 skeletal isomerization selectivity were observed. At the low CO conversions, the 1-butene conversions were very small ($>1\%$). At the high CO conversions, the conversion of the 1-

butene was between 26 and 57%. Of the 1-butene reacted about 60% formed 2-butene, and 30% n-butane. The remaining 10% may have been converted to some extent to higher hydrocarbons, as indicated by Figures 7 and 8. In Figure 7 a slight increase in C_5 selectivity is seen with increased 1-butene partial pressure at each set of conditions. Figure 8 is a Flory plot excluding C_4 products, for low and high 1-butene partial pressures. There appears to be a slight increase in the selectivity to form C_5-C_7 products relative to the C_1-C_3 products with an increased 1-butene partial pressure. However, there is no change in α.

1-Hexene

The addition of 1-hexene with varying CO conversions did not significantly affect the CO or the H_2 conversions, methane selectivity, olefin/paraffin or α-olefin/β-olefin ratios. Only a slight increase was observed in the C_6 skeletal isomer selectivity. n-Hexane and 2-hexene were formed in essentially equal amounts at both high and low CO conversions. At a CO conversion of 26% only about 15% of the 1-hexene reacted and there was no change in the selectivity to form C_7-C_{10} products relative to C_1-C_5 products.

At a CO conversion of 90% (0.92 MPa), 70% of the 1-hexene in the feed reacted, and there seemed to be an increase in the C_7-C_{10} products. This is shown in Figure 9, a Flory plot of C_1-C_{10} products excluding C_6 for three experiments conducted, two with 1-hexene feed addition and one without. 75% of the 1-hexene that disappeared formed hexane or β-olefin. 25% was unaccounted for. Although the results in Figure 9 indicate considerable incorporation of hexene into growing chains we are uncertain how reliable these results are. In our analytical system the C_6-C_{10} products are distributed between a liquid phase in a trap and a gas phase, the analytical results of which are combined. During 1-hexene addition the C_7-C_{10} products are present in relatively small concentrations in the liquid compared to C_6 which also reduces the accuracy with which they could be determined. We are inclined to believe that the enhanced formation of C_7-C_{10} was a real effect, but that the change in slope with increased hexene content may well have been an artifact.

<u>1-Decene</u>

As with the 1-butene and 1-hexene, the addition of 1-decene to the feed stream at high CO conversion did not significantly affect the H_2 or CO conversions, methane selectivity, the olefin/paraffin ratio, the α-olefin/β-olefin ratio, or the C_9 hydrocarbon selectivity. The selectivity to form C_{10} skeletal isomer, defined as the ratio of the rate of C_{10}-isomer production to the rate of CO consumption, increased from 3.7×10^{-4} to 20.4×10^{-4}.

The conversion of the 1-decene in the feed was 81%. Of this, 24% formed n-decane, 43% formed 2-decene, 10% formed C_{10}-isomer, and the remaining 23% was unaccounted for. Shown in Figure 10 are Flory plots for the results with and without 1-decene in the feed. The selectivity to form C_{10}^+ products increased slightly upon the addition of 1-decene to the feed. The partial pressure of added decene was much lower than that of the lower olefins; more evidence of chain incorporation might have appeared at higher concentrations.

1-Eicosene

6.5 grams of 1-eicosene were added to the reactor after 50 hours of synthesis, and the synthesis was then continued for an additional 8 hours. The amount of C_{20} compounds vaporized from the reactor was negligible.

Listed in Table 4 are the calculated number of moles of 1-eicosene and n-eicosane plus 2-cis-eicosene (these two compounds could not be split by the g.c.) in the reactor before, immediately after, and 8 hours after the addition of 1-eicosene. The 1-eicosene molar quantity was increased markedly by the addition, from 0.15×10^{-3} to 13.89×10^{-3} moles. This latter quantity corresponds to 3.9 grams of 1-eicosene, about 2.6 grams less than the added amount. As seen in Table 4, a fraction of the 1-eicosene was hydrogenated and isomerized immediately to n-eicosane and 2-cis-eicosene, respectively. However, this conversion was not nearly enough to account for the missing 1-eicosene. The lack of closure on the 1-eicosene balance may have been due to the difficulty in accurately determining the absolute molar quantity of a compound when another compound, in this case octacosane, is present in large excess (>90 wt% of reactor wax).

After 8 hours of synthesis, the number of moles of 1-eicosene had decreased significantly (~76% conversion) while the moles of n-eicosane plus cis-2-eicosene increased by an almost proportional amount; the total number of moles of the 3 compounds decreased from 16.93×10^{-3} to 16.28×10^{-3} after 8 hours of synthesis, which is probably within the experimental error of the analysis.

Some incorporation did occur, as shown in Figure 11, where the absolute numbers of C_{17}-C_{25} moles in the reactor wax, excluding 1-eicosene, are shown on a Flory plot for the samples taken initially and after 8 hours of synthesis. The C_{21}-C_{25} molar quantities increased about 20-25% while the C_{17}-C_{19} quantities remained essentially constant.

Discussion - Olefins

An overview of the reaction pathways of normal α olefins is presented by the data and calculations in Table 5. This summarizes the results of seven representative olefin feed addition experiments. The first four listed were conducted at high CO conversion (low p_{CO}), while the final three were conducted at low CO conversion (high p_{CO}). Included in the table are calculated rate constants for the three most pertinent reactions involving the added 1-olefin: (1) the consumption of the 1-olefin (largely to the corresponding β olefin and paraffin), (2) the formation of the corresponding paraffin, and (3) in the cases of 1-butene, 1-hexene, and 1-decene, the formation of the corresponding β-olefin (trans- plus cis-2-olefin).

For comparative purposes, reaction rate constants were calculated by assuming the following simple rate equations:

α-Olefin disappearance: $C{=}C{-}R \xrightarrow{k_1} \text{Products},\ -r = k_1 p_{C=C-R}$ (3)

Paraffin production: $C{=}C{-}R + H_2 \xrightarrow{k_2} C{-}C{-}R,\ r = k_2 p_{H_2} p_{C=C-R}$ (4)

β-Olefin production: $C{=}C{-}R \xrightarrow{k_3} C{-}C{=}R,\ r = k_3 p_{C=C-R}$ (5)

The olefin partial pressure used in Equations 3, 4 and 5 was the total partial pressure of the olefin in the reactor. The rate of reaction is that found after subtracting the rate observed in the base case experiment.

Also shown in Table 5 are the percent conversion of the olefin in the feed and the percent of the olefin added that was converted to paraffin, to β-olefin, to skeletal isomers, to incorporation products, and to that which was unaccounted for. The incorporation products are taken to be the increase in hydrocarbons that contain 1 carbon atom more than the olefin additive.

The rate constants for the three reactions are consistently higher at the lower values of p_{CO} for each olefin studied. This supports the finding of Sudheimer and Gaube (9) that the hydrogenation and isomerization reaction rates of 1-hexene and 1-decene during Fischer-Tropsch synthesis over an iron catalyst were inversely proportional to p_{CO}.

Ethylene is clearly more reactive than 1-butene. Schulz et al. (10) added ethylene and propylene to the Fischer-Tropsch synthesis feedstream and under similar conditions found that 76% of the ethylene was consumed as compared to 44% of the propylene. In an earlier study (11) we observed that while from 18% to 32% of the ethylene added to the Fischer-Tropsch synthesis feedstream was hydrogenated to ethane, less than 0.5% of the added 1-butene was hydrogenated to n-butane under similar synthesis conditions.

The drop in reactivity from ethylene to 1-butene is however reversed as higher olefins are considered. The rate constants for reaction 1 decrease in the following order: 1-decene > 1-

hexene $\gtrsim$ ethylene > 1-butene. For olefin hydrogenation the order of decreasing activity is ethylene > 1-decene > 1-hexene > 1-butene. For $\alpha \rightarrow \beta$-olefin isomerization activity the order is 1-decene > 1-hexene > 1-butene. These findings suggest then that the reactivity of the primary olefins increases with increasing molecular weight, the exception being ethylene. This probably reflects that fact that, other factors being equal, the degree of adsorptivity increases with molecular weight.

For present reaction conditions, at low values of p_{CO} the quantity of olefins hydrogenated is somewhat greater than the quantity isomerized. At the higher values of p_{CO}, the quantities are about equal.

Skeletal isomerization of the added olefin was small relative to $\alpha \rightarrow \beta$ isomerization and hydrogenation. No detectable amount of any of the olefins was cracked as was evidenced by the lack of increase in the rate of formation of hydrocarbons containing one carbon atom less than the added olefin. Absence of these reactions was also observed in other studies. As discussed by Dry (12), Kölbel et al (13) found that hydrocracking over an Fe catalyst accounted for less than 3 percent of the CH_4 produced at temperatures up to 573°K, and Forney (14) reported that with iron catalysts the oil was not cracked until temperatures were in excess of 573°K. We (11) found no evidence for the skeletal isomerization of 1-butene nor for the cracking of ethylene or 1-butene. Likewise, Dwyer and Somorjai (15) did not find cracking of ethylene or propylene to occur. Hall et al. (16) concluded that hydrocracking of ethylene is unimportant, and

Schulz et al. (10) reported that less than 1% of the added ethylene or propylene cracked under the conditions of their study.

The low degree to which olefin incorporation occurs relative to hydrogenation and $\alpha \rightarrow \beta$ isomerization is noteworthy. (This result is also evident from the 1-eicosene data shown in Table 4 where of the 76% of 1-eicosene converted, about 94% formed n-eicosane and 2-eicosene.) The reaction of the olefins with surface methylene ($-CH_2-$) species is indicated in Figure 4 for ethylene and in Figure 6 for 1-butene. The selectivity to form C_3 hydrocarbons is seen to increase with increasing $P_{C_2H_4}$, (Figure 5) and the selectivity to form C_5 hydrocarbons increases with increasing $P_{C_4H_8}$ (Figure 6). Again, for 1-hexene, the selectivity to form hydrocarbons containing more than 1 additional carbon atom above the number of carbon atoms in the olefin also increased (Figure 8). All these results suggest then that the primary olefin can act as a chain initiator or that it could directly react as a chain terminator with surface species larger than methylene. Evidence for the chain initiation reaction involving ethylene is shown in Figure 4, where the added ethylene did not significantly affect the C_3-C_7 chain growth probability.

In contrast to these results are the results of Schulz et al. (10) and Dwyer and Somorjai (15). Schulz et al. (10) observed a chain-termination reaction with ethylene. When ethylene-C^{14} was added to the synthesis gas, the molar radioactivity of the C_3 and greater reaction products decreased rapidly with the C number. Dwyer and Somorjai (15) found that the chain growth probability increased with the addition of ethylene to the feed stream and concluded that ethylene participates in chain propagation. However, we (11) pointed out that the results may have been magnified by a combination of low conversion ($x_{CO} < 1\%$), lack of alkali promoter in the catalyst, unsteady-state activity and catalyst phase composition in their experiments.

The 1-butene feed addition caused the C_5-C_7 to increase very slightly, relative to C_1-C_5 products.

1-Hexene seemed to show a much more pronounced effect than 1-butene (Figure 9), but we think this was at least in part an experimental artifact. Added 1-decene only slightly increased the selectivity to form C_{11}-C_{14} products relative to C_1-C_9 products (Figure 10), but the concentration of added decene was quite low. With the addition of 1-eicosene, selectivity to form C_{21}-C_{25} products relative to C_{17}-C_{19} products increased only slightly (Figure 11). In this case also the concentration of the added 1-olefin was quite low.

An increase in the partial pressure of ethylene is seen to decrease methane selectivity (Figure 2) and increase the C_3 and C_4 olefin/paraffin ratios (Figure 3). With increasing ethylene concentration there is an associated decrease in the hydrogenating character of the catalyst. Dwyer and Somorjai (15) also observed a slight inhibition of methanation at high ethylene partial pressures. No significant effects of 1-butene, 1-hexene, and 1-decene, on the above product distribution characteristics were observed.

It is noteworthy that with all the olefins the CO conversion remains essentially constant with increased olefin partial pressure. This suggests that CO is much more strongly adsorbed than the olefins. Presumably they compete for the same sites, since the secondary reactions of olefins increase markedly at low CO concentrations, corresponding to high conversions.

Increased ethylene partial pressure causes an increase in the formation of 1-propanol and 2-butanone. This suggests that ethylene reacts with adsorbed oxygenated species by reactions such as

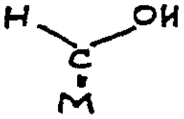
$$C_2H_4 + CH_2OH^* \rightarrow C_3H_7OH \qquad (6)$$

$$C_2H_4 + CH_3CH_2OH^* \rightarrow C_2H_5COCH_3 \qquad (7)$$

The fact that 2-butanone is formed instead of 1-butanol suggests that the iron-carbon bond is formed with the oxygenated carbon.

A similar phenomenon was observed by Pijolat and Perrichon (17). In their studies using a 10 wt% Fe on τ-alumina in a microreactor at 225°C and 18 bars, they observed a five-fold increase in the formation of n-pentanol-1 upon the addition of n-butene-1 to a H_2/CO (2/1) feed. They also observed a lesser enhancement of n-hexanol-1 and possibly n-pentanol-2 and n-hexanol-2. They proposed that the increased n-pentanol-1 formation was caused by the insertion of CO into the adsorbed n-butene-1, followed by hydrogenation. To support their hypothesis, they noted an earlier study of theirs (18) wherein they used I.R. spectroscopy to reveal the presence of non-dissociated CO on the metallic iron sites of their Fe/Al_2O_3 catalyst after reaction at 14 bars and 300°C.

The existence of oxygen-containing species on the catalyst surface has been hypothesized since 1951, when Anderson (19) proposed a mechanism based on an enolic intermediate:



However, as later pointed out by Anderson (20), since the mid-1950's no substantial evidence has been reported that supports the enolic intermediate scheme for the Fischer-Tropsch synthesis. In fact, in an encompassing review by Biloen (21), strong arguments are presented in support of a mechanism based on a hydrogenated carbon intermediate.

* * *

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Figure Captions

Figure 1	Ethanol addition has no effect on Flory distribution except for methane. Data normalized excluding C_2 fraction. Total pressure = 0.92 MPa.
Figure 2	Ethylene addition decreases methane selectivity.
Figure 3	Ethylene addition increases olefin/paraffin ratio. Legend shown on Figure 2.
Figure 4	Ethylene addition has no significant effect on Flory distribution except for methane. Data normalized excluding C_2 fraction. Total pressure = 0.92 - 0.98 MPa, 248°C, high CO conversions.
Figure 5	The effect of ethylene on formation of propane plus propene. Total pressure = 0.78 - 1.58 MPa. Legend shown on Figure 2.
Figure 6	Ethylene increases 1-propanol selectivity. Total pressure = 0.78 - 1.58 MPa. Legend shown on Figure 2.
Figure 7	The effect of 1-butene on formation of C_5 hydrocarbons. Oxygenates excluded. Total pressure = 0.78 - 1.58 MPa. Legend shown on Figure 2. ■ points correspond to $p_{CO} = 0.46 - 0.49$ MPa and $p_{TOT} = 1.48$ MPa.
Figure 8	1-Butene addition slightly increases C_5+ fraction. Overlapping points at C_2 and C_3. Data normalized excluding C_4 fraction. Total pressure = 0.92 - 0.95 MPa.

Figure 9	1-Hexene addition increases C_7+ fraction. Overlapping points at each of C_1-C_5. High CO conversions. Data normalized excluding C_6 fraction. Total pressure = 0.92 MPa.
Figure 10	1-Decene addition slightly increases C_{11}+ fraction. Overlapping points at C_2 and C_{13}. Data normalized excluding C_{10} fraction. Total pressure = 0.92 MPa.
Figure 11	1-Eicosene addition moderately increases C_{21}+ fraction. Data normalized excluding C_{20} fraction. Total pressure = 0.92 MPa.

Table I - Compounds Studied

Compound	Description
Ethanol	200 proof (U.S. Industrial Chemicals)
Ethylene	2 sets of premixed tanks (Matheson), 0.92 H_2/CO, 1.6 or 8.6 mol% ethylene
1-Butene	2 sets of premixed tanks (Matheson), 0.92 H_2/CO, 0.99 or 4.9 mol% 1-butene
1-Hexene	99.9% (Aldrich)
1-Decene	99% (Alfa Products)
1-Eicosene	98.5% (Wiley Organics)

Table 2. Experimental Results for all Feed Addition Experiments[a]

Species	% Conversion without additive CO	% Conversion without additive H_2	% Conversion with additive CO	% Conversion with additive H_2	Partial Pressure of Species in Exit, kPa without additive	Partial Pressure of Species in Exit, kPa with additive	Total Pressure, MPa
Ethanol	40	26	42	27	1.0	33	0.92
	89	65	89	59	2.0	35	0.92
			88	56		58	
	93	68	89	59	2.0	46	0.92
Ethylene	27	21	29	23	2.0	15	0.78 - 0.79
			29	25		78	0.84
	86	63	90	67	3.0	6.0	0.78 - 0.79
			85	70		47	0.84
	92	69	94	73	5.0	28	1.48 - 1.49
			94	79		84	1.58
	93	68	91	73	5.0	68	0.92 - 0.98
1-Butene	27	21	31	24	1.0	10	0.78
			31	24		48	0.81
	86	63	90	66	5.0	11	0.78
			88	66		42	0.81
	38	31	42	34	3.0	24	1.48
			40	33		98	1.52
	91	69	91	71	13.0	34	1.48
			89	69		118	1.52
	93	68	92	67	8.0	62	0.92 - 0.95
1-Hexene	26	19	27	20	0.4	28	0.92
	91	67	89	65	1.2	11	0.92
			90	66		17	
1-Decene	95	70	94	68	0.2	4.4	0.92
1-Eicosene[b]	92	65					

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[a] 248°C, $(H_2/CO)_{feed} = 0.90 - 0.97$

[b] 6.5 g of 1-eicosene injected into reactor containing about 400 g octacosane.

Table 3 - Selectivity results from ethanol feed addition experiments (248°C, 0.92 MPA, 0.90–0.94 H_2/CO).

	CO Conversion = 88 – 93%					CO Conversion = 40-42%	
P_{H_2}, kPa	298	310	307	280	299	407	395
P_{CO}, kPa	97	93	90	67	86	367	346
P_{CO_2}, kPa	385	353	313	402	342	110	113
P_{H_2O}, kPa	26	36	59	35	34	12	9
P_{EtOH}, kPa	2	35	58	2	46	1	33
Vol. % EtOH in Feed	—	3.1	6.4	—	4.0	--	2.9
Conversion of EtOH in Feed (%)	—	29	38	—	28	--	1.0
	Moles Product per Mole CO Consumed (x 100)						
Methane	5.5	3.7	3.5	5.0	4.2	3.1	2.6
Ethylene	0.37	0.78	1.00	0.6	1.5	0.97	1.08
Ethane	2.0	1.5	1.3	1.9	1.3	0.54	0.43
Ethylene + Ethane	2.4	2.2	2.3	2.5	2.8	1.5	1.5
Propylene + Propane	2.6	2.3	2.3	2.7	2.8	1.4	1.3
Ethanal (Acetaldehyde)	0.01	0.18	0.35	0.01	0.10	0.04	0.36
Ethylacetate	0.00	0.17	0.30	0.00	0.29	0.00	0.02
Propanal + Propanone	0.03	0.17	0.25	0.08	0.28	0.03	0.11
CO_2	46.9	46.8	46.4	47.1	49.3	45.1	44.4
Olefin/Paraffin C_2	0.19	0.52	0.77	0.33	1.15	1.8	2.5
C_3	1.9	4.0	4.7	3.4	6.7	4.6	4.8
C_4	2.6	4.0	4.6	3.7	6.0	4.0	4.2
α-Olefin/β-Olefin C_4	1.7	5.3	8.0	2.8	13.4	17.0	28.0
C_5	1.7	5.7	9.0	2.7	12.9	20.0	35.0

Table 4 - Molar quantities of C_{20} compounds before and after 1-eicosene addition to the reactor[a].

Moles x 10^3	Initial	Immediately after Addition	After 8 hours of Synthesis
1-Eicosene	0.15	13.89	3.35
n-Eicosane + 2-cis-Eicosene	2.48	3.04	12.93
TOTAL	2.63	16.93	16.28

---

[a] 248°C, 0.92 MPa, x_{CO} = 0.92.

Table 5 - Reaction Pathways for Primary Olefins (248°C)

Olefin Feed Additive	P_{CO} MPa	P_{H_2} MPa	Vol % Olefin in Feed	Reaction Rate Constants for Olefin Reactions			% Conversion of Olefin	% Olefin in Feed Converted to:				
				k_1 [a]	k_2 [b]	k_3 [c]		Paraffin	β-Olefin	Isomer[d]	Incorporation[e]	Unaccounted for[f]
Low CO Partial Pressure:												
Ethylene	0.080	0.23	8.6	235	820	--	59	47	--	--	4	5
1-Butene	0.071	0.27	4.9	99	130	72	38	13	28	0.0	0.9	-3.9
1-Hexene	0.090	0.28	3.7	231	230	76	74	20	24	0.5	1.2	28
1-Decene	0.054	0.28	1.3	663	570	285	81	19	35	8	0.0	19
High CO Partial Pressure:												
Ethylene	0.34	0.33	8.6	107	300	--	9.2	10	--	--	0.6	0.4
1-Butene	0.57	0.59	4.9	0.0	10	9	<1	(g)	(g)	0.0	0.0	0.0
1-Hexene	0.39	0.41	3.2	163	60	36	15	2	2	0.0	0.1	10.9

---

[a] k_1 = (rate olefin consumption)/P_{olefin} [μ moles/min-gm cat. (unreduced basis)-MPA]

[b] k_2 = (rate paraffin product)/P_{H_2} P_{olefin} [μ moles/min-gm cat. (unreduced basis)-MPa^2]

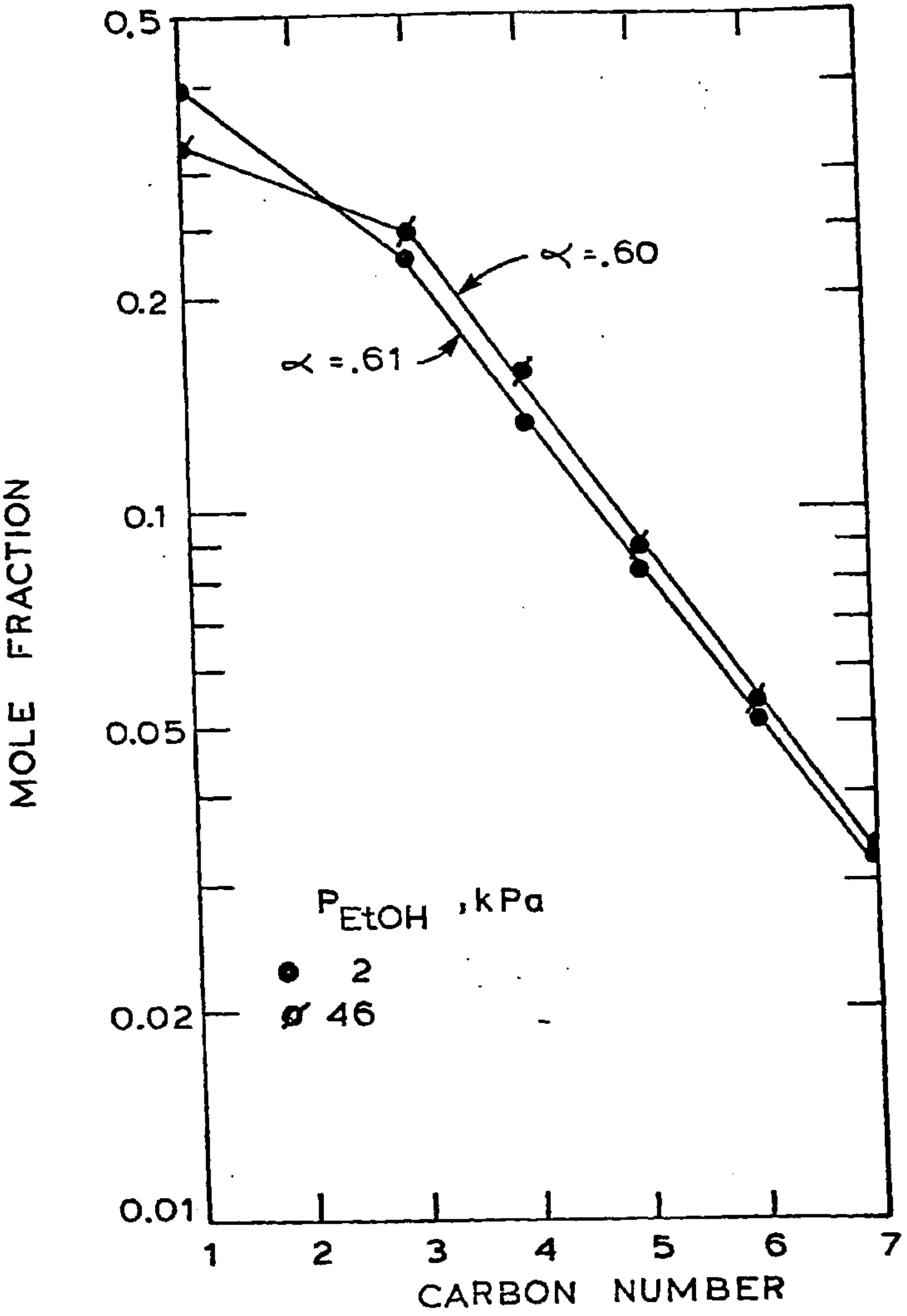
[c] k_3 = (rate β-olefin production)/P_{olefin} [μ moles/min-gm cat. (unreduced basis)- MPa]

[d] Isomer formation at same carbon number as olefin additive

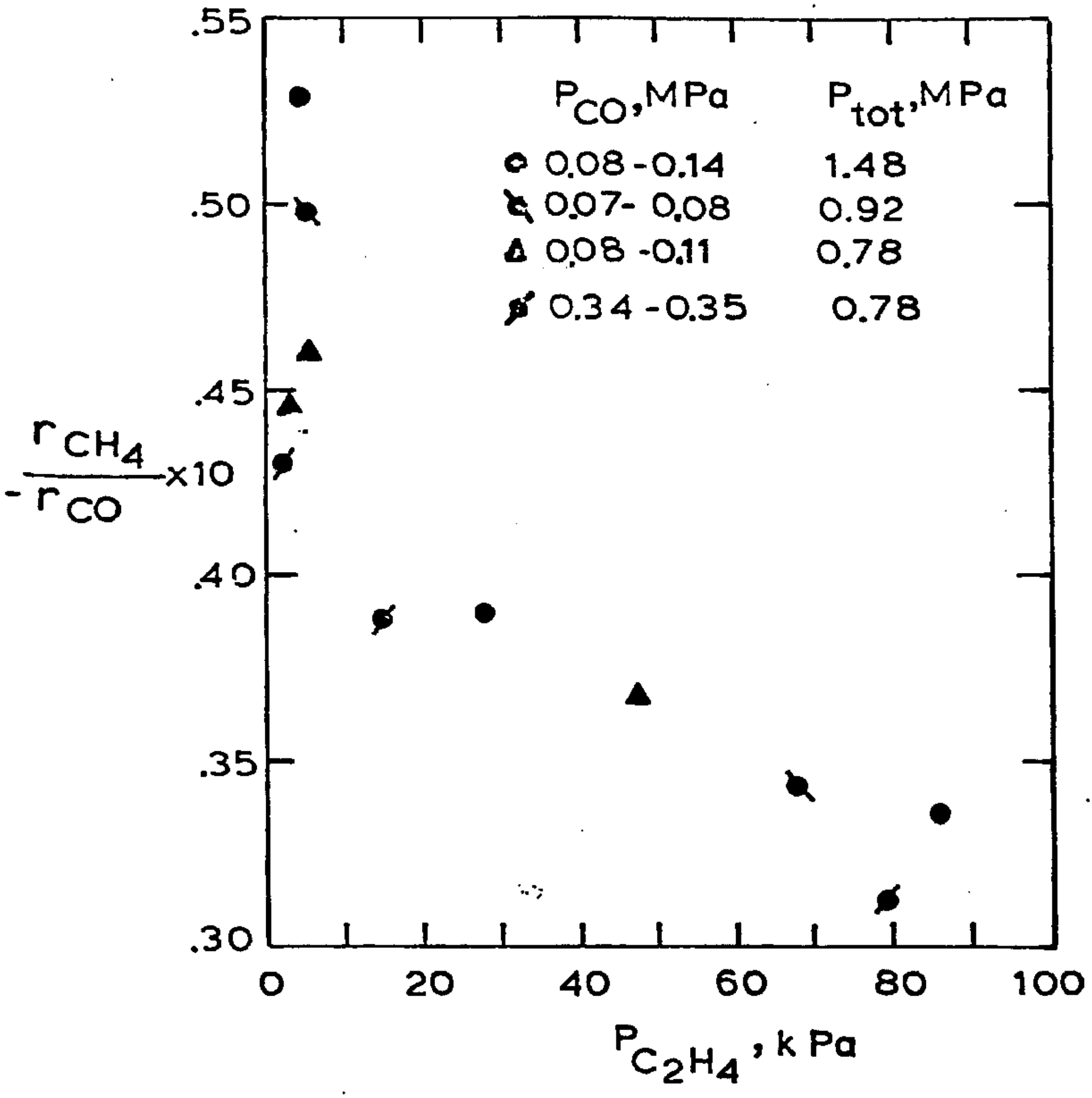
[e] Formation of hydrocarbons containing 1 carbon atom more than the olefin additive

[f] % Unaccounted = (% Olefin Conversion) - % Olefin converted to paraffin, β-olefin, isomer and incorporation.

[g] The ratio of paraffin to β-olefin was about unity.

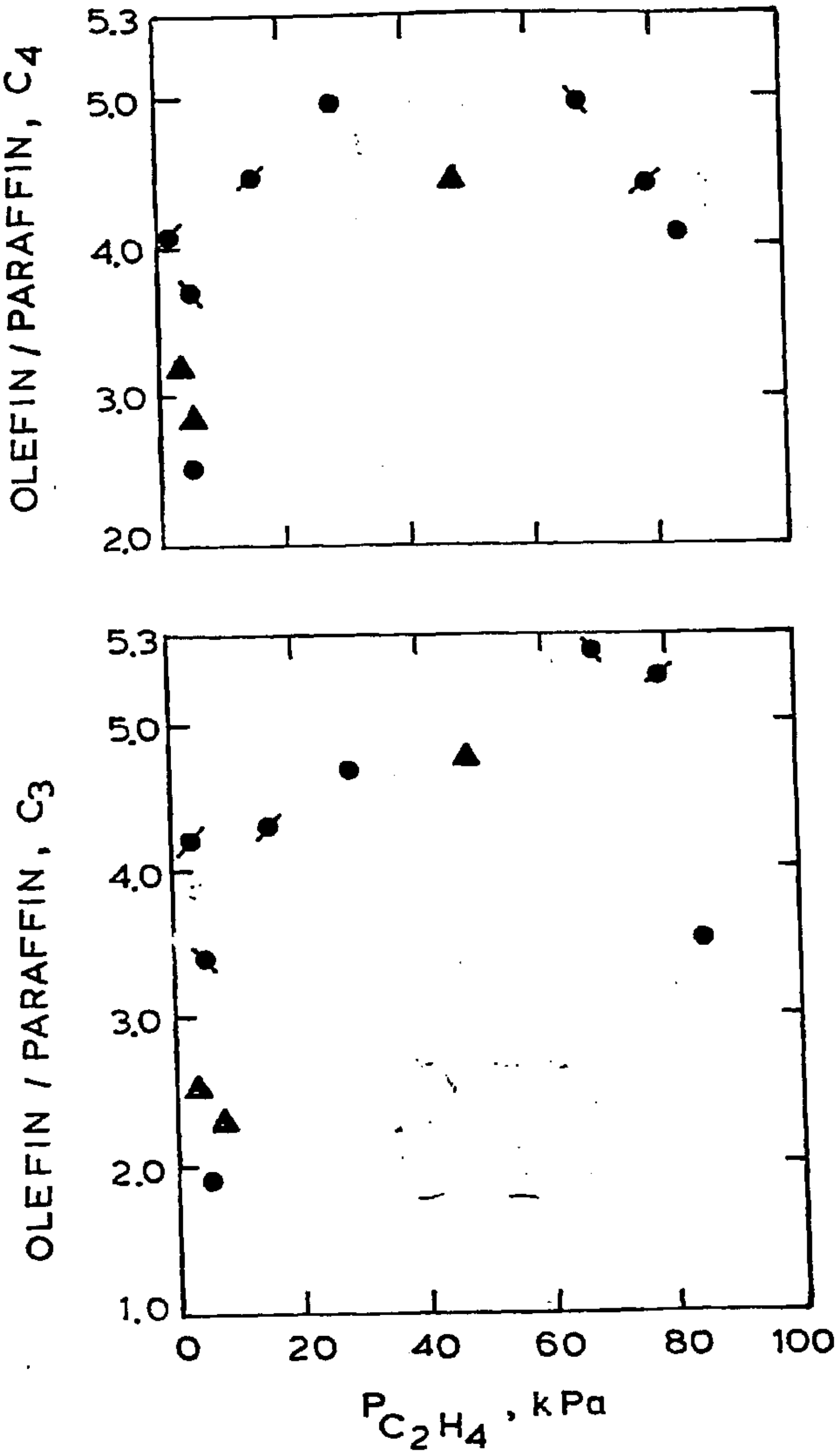

0.5
0.2
0.1
0.05
0.02
0.01
MOLE FRACTION
1
2
3
4
5
6
7
CARBON NUMBER
α =.60
α =.61
P_{EtOH} ,kPa
● 2
ø 46

①



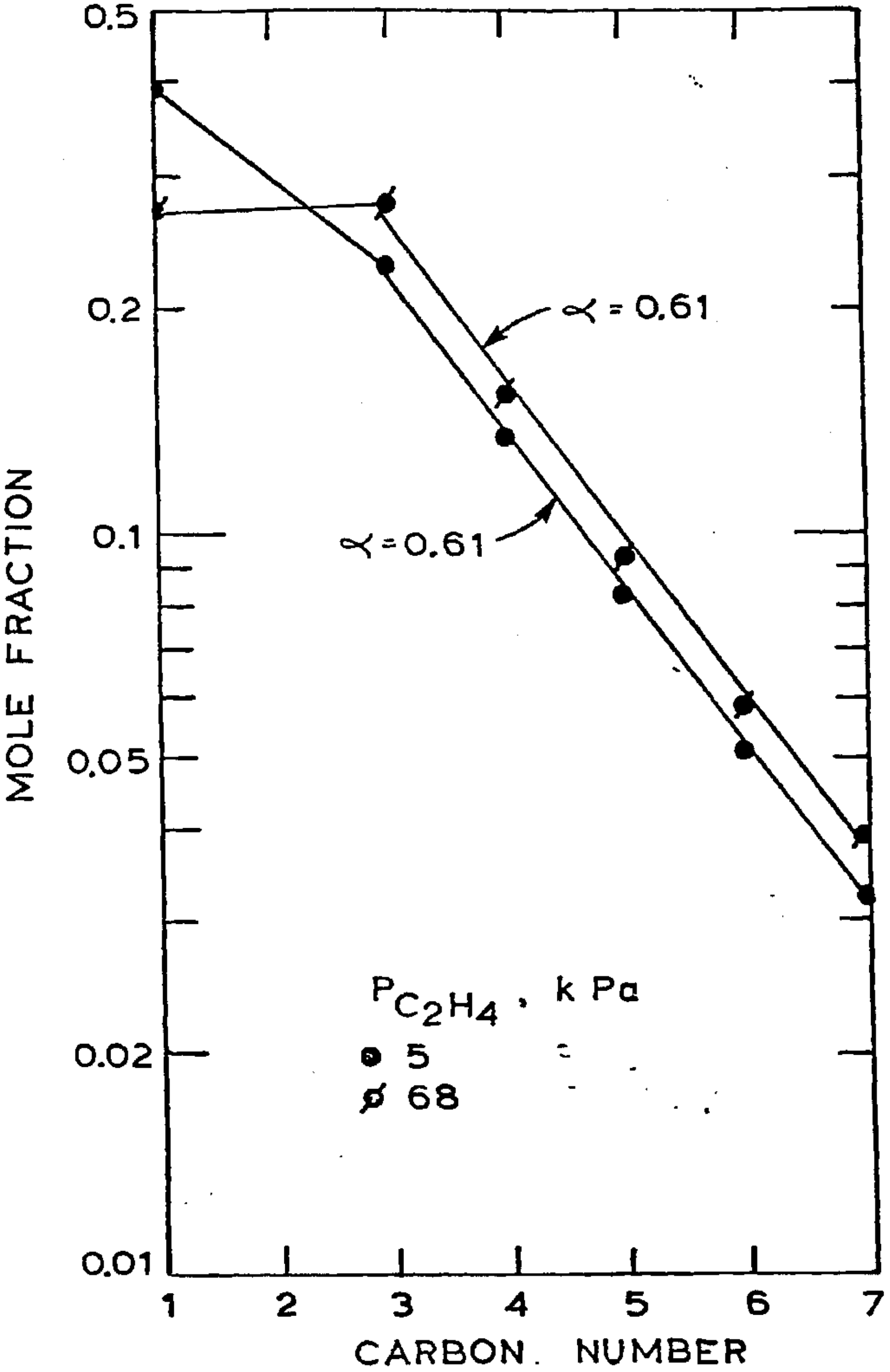
P_{CO}, MPa
P_{tot}, MPa
● 0.08-0.14 1.48
0.07-0.08 0.92
▲ 0.08-0.11 0.78
0.34-0.35 0.78
$\frac{r_{CH_4}}{-r_{CO}} \times 10$
.55
.50
.45
.40
.35
.30
0
20
40
60
80
100
$P_{C_2H_4}$, kPa

②



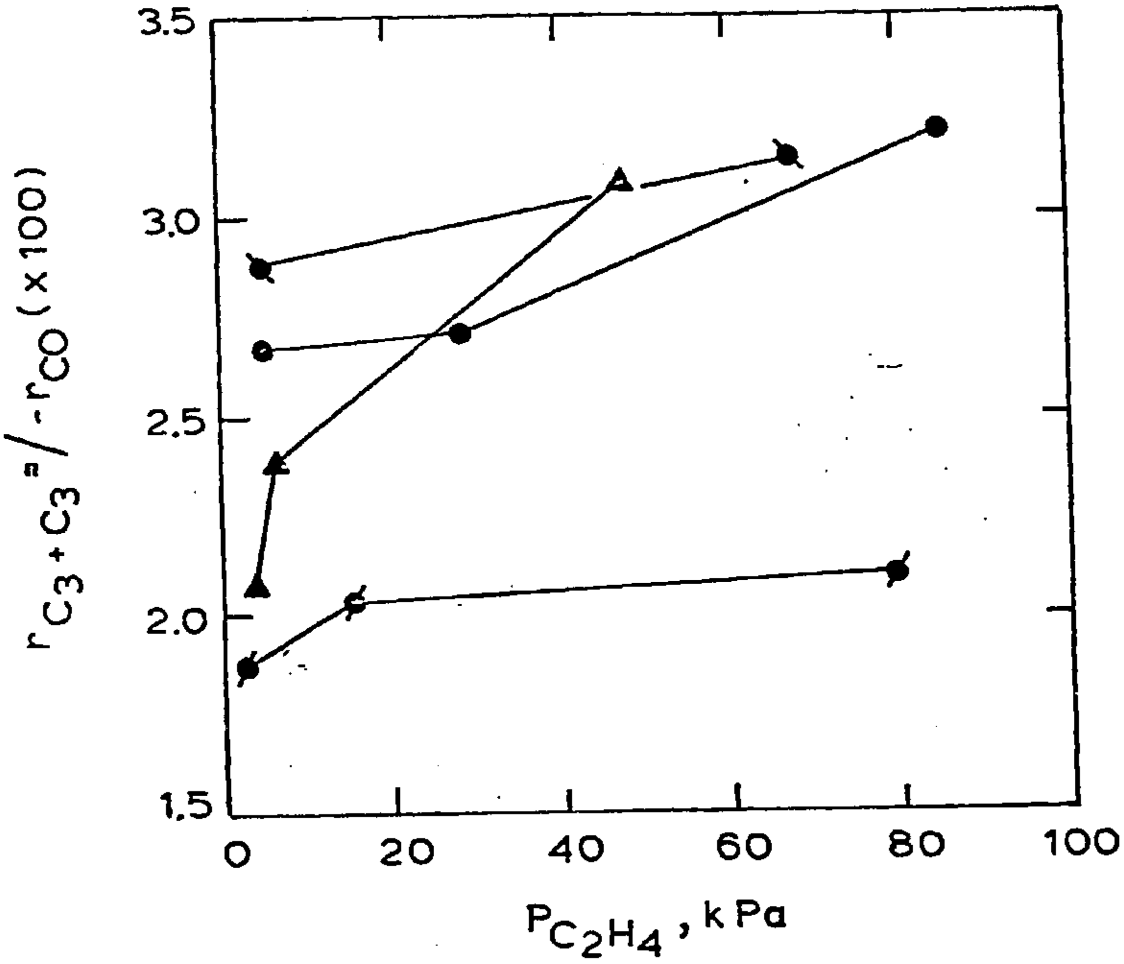
5.3
5.0
4.0
3.0
2.0
OLEFIN / PARAFFIN, C_4
5.3
5.0
4.0
3.0
2.0
1.0
OLEFIN / PARAFFIN, C_3
0
20
40
60
80
100
$P_{C_2H_4}$, kPa

③



0.5
0.2
0.1
0.05
0.02
0.01
MOLE FRACTION
1
2
3
4
5
6
7
CARBON. NUMBER
α = 0.61
α = 0.61
$P_{C_2H_4}$, k Pa
● 5
ø 68

④



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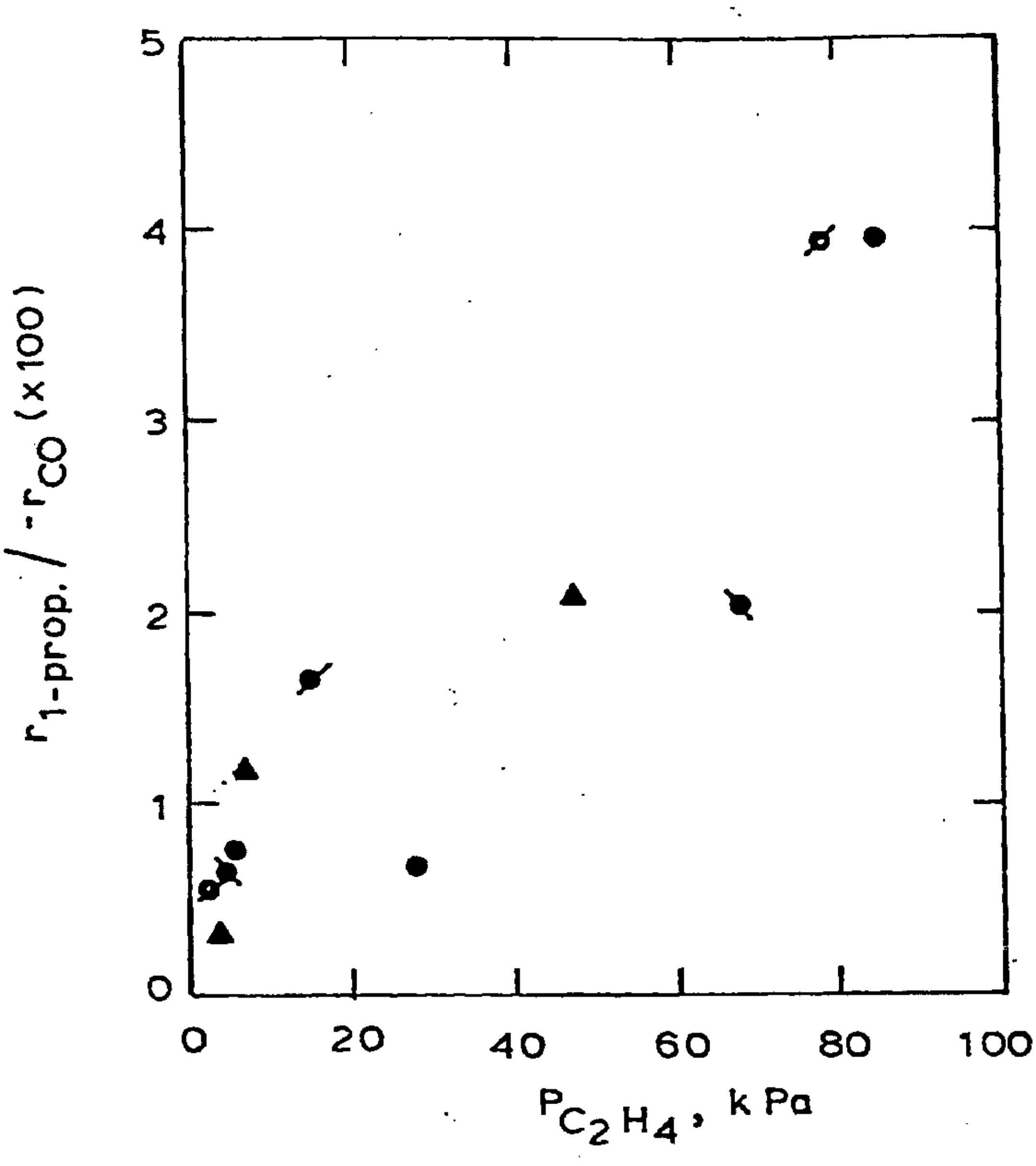

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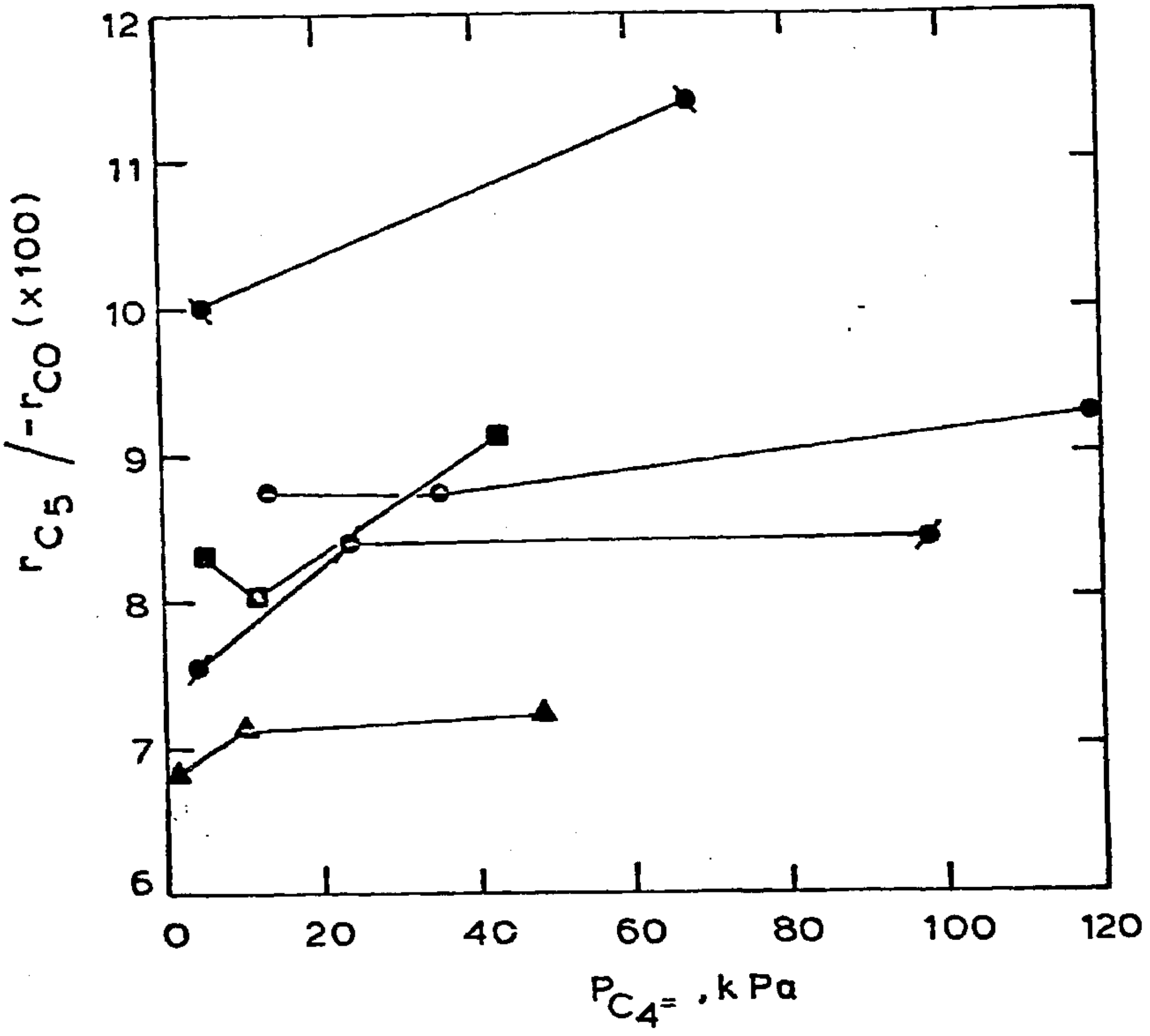

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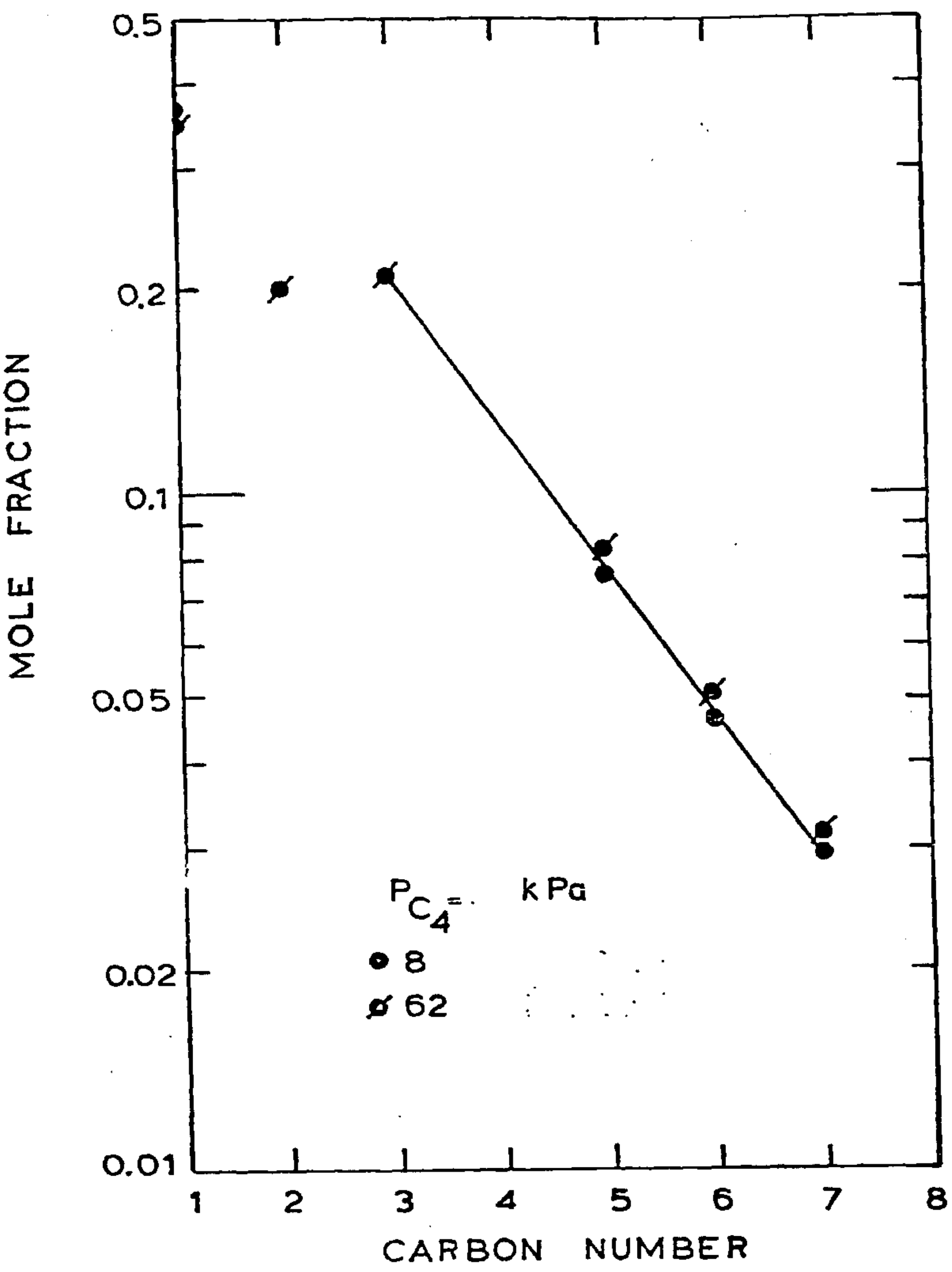

0.5
0.2
0.1
0.05
0.02
0.01
MOLE FRACTION
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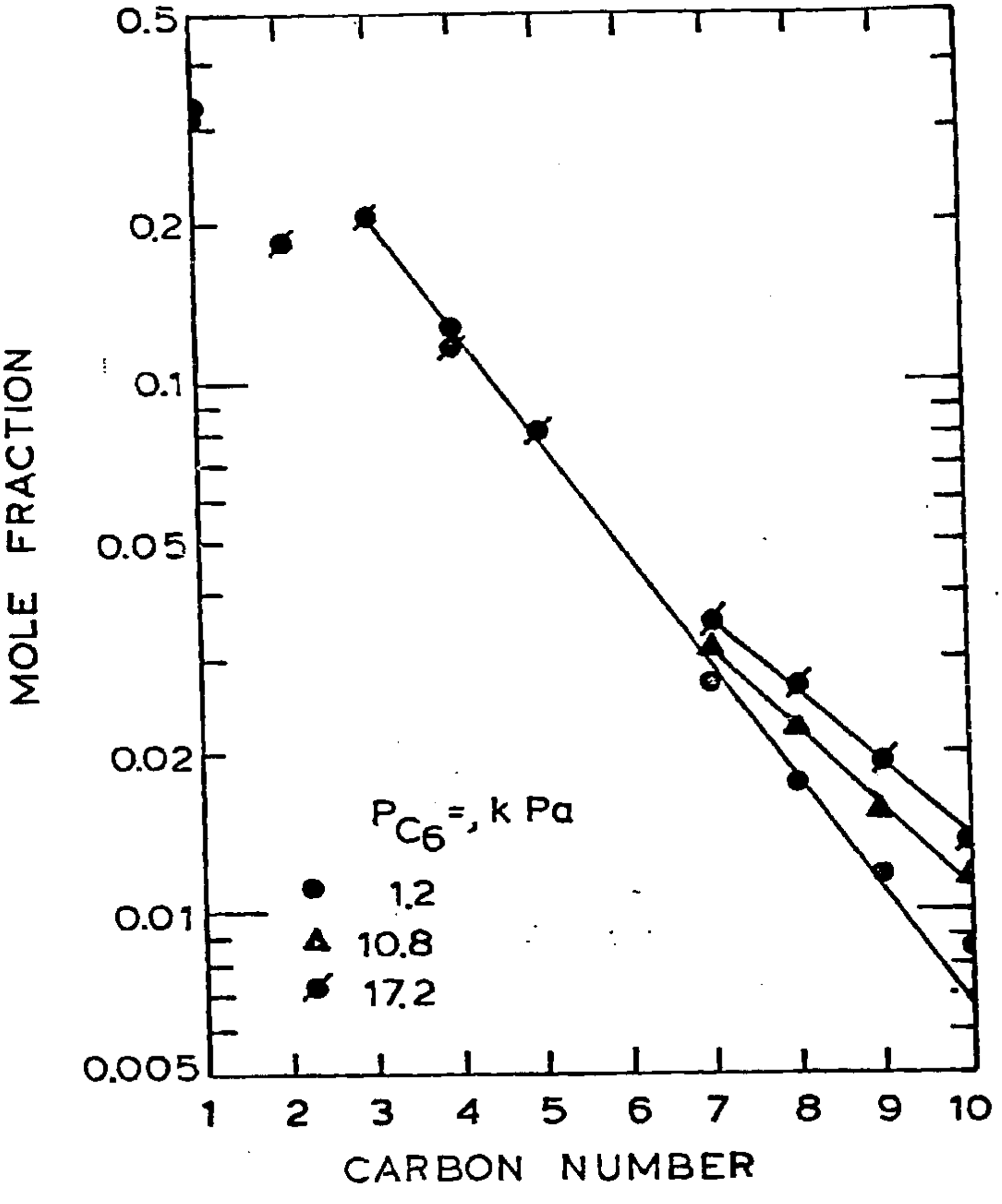
7
8
CARBON NUMBER
$P_{C_4^=}$, kPa
● 8
ø 62

(8)



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0.005
MOLE FRACTION
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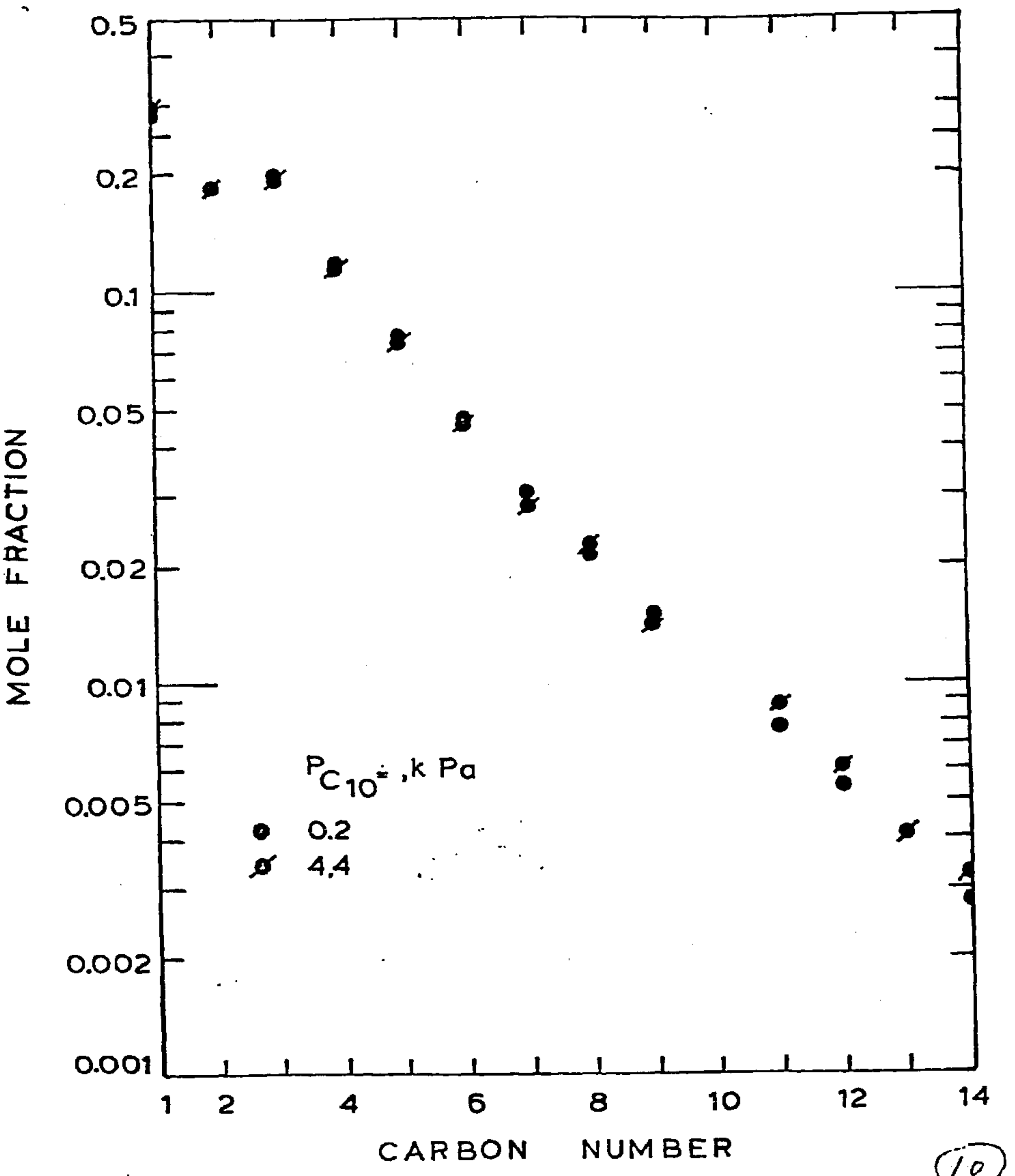
5
6
7
8
9
10
CARBON NUMBER
$P_{C_6^=}$, k Pa
● 1.2
▲ 10.8
● 17.2

⑨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0.02
0.01
0.005
0.002
0.001
MOLE FRACTION
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4
6
8
10
12
14
CARBON NUMBER
$P_{C_{10}^{=}}$, k Pa
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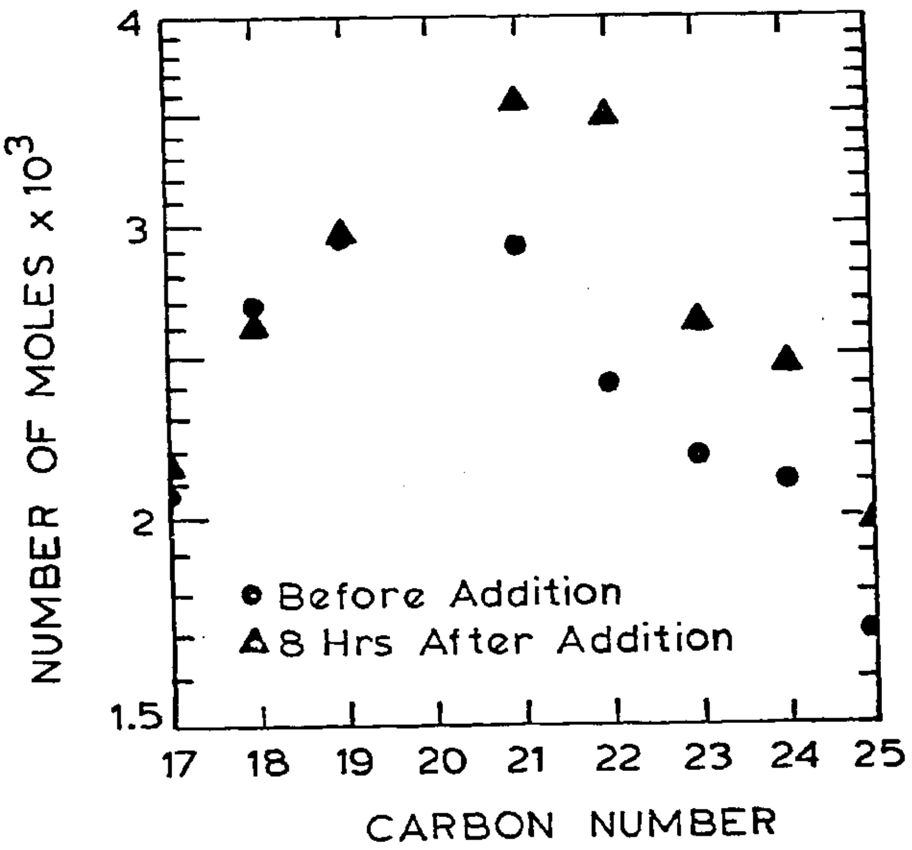
ø 4.4

⑩


NUMBER OF MOLES x 10^3
4
3
2
1.5
17
18
19
20
21
22
23
24
25
CARBON NUMBER
● Before Addition
▲ 8 Hrs After Addition

11