the fraction of methanol produced at various pressures are presented in section 4.4.

4.2.3 Effect of water vapor in feed stream for the FeCo catalyst

In section 4.1, it was suggested that the decrease in CO activity with increasing conversion might be inhibition due to water blocking active synthesis sites. In an attempt to observe this effect an experiment was performed using the FeCo catalyst in which the effect of feed stream water on CO activity and water gas shift activity was observed. The catalyst was brought to steady state reaction conditions at 7.8 atmosphere using the 1/3 feed and several rate measurements were obtained over a range of CO conversions (.5 to 6%) using the silica trap immersed in a dry ice/acetone bath in order to remove any water in the feed stream. Immediately after these measurements the cold bath was removed and the trap was allowed to heat up to room temperature. At the time that the trap was removed the gas hourly space velocity was fixed so that the CO conversion was less than 1%. Figure 4.2.5 shows the effect of the water vapor in the feedstream on the shift activity compared to the activity obtained with the cold trap. The data obtained at less than 1% conversion were obtained first and the very high shift activity associated with these data points is most likely due to the high content of the water vapor present in the feed gas when the trap initially warms up. The amount of water in the gas stream could not be quantatively determined (Section 3.3). However during trap warm up the water mole fraction was approximately five times higher (.005) than that typically observed at 1% CO conversion. Higher conversion data were obtained at successively later times. Although this experiment can yield no
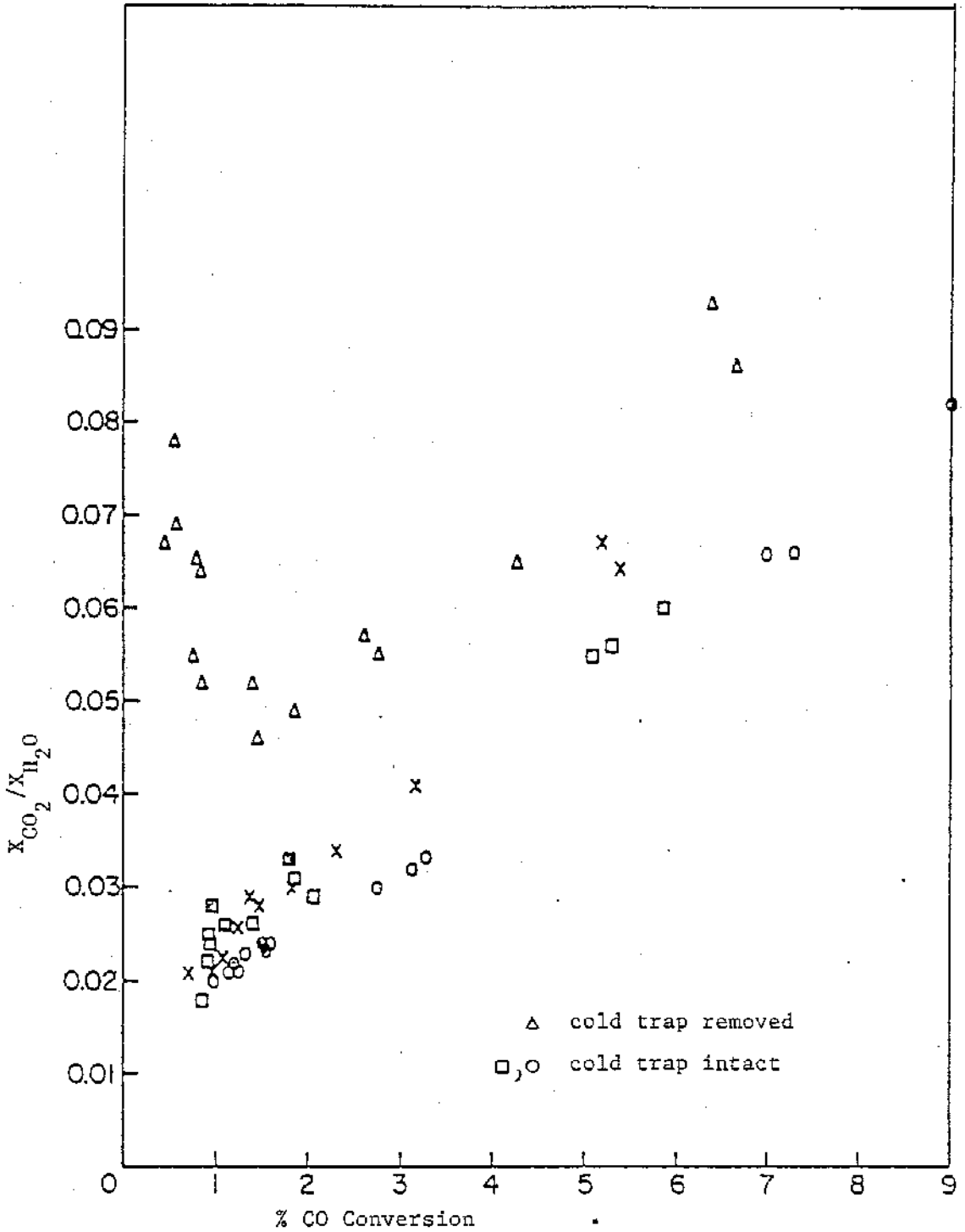
Figure 4.2.5 X_{CO_2}/X_{H_2O} versus % CO conversion for the FeCo catalyst at 7.8 atmospheres with the 1/3 CO/H_2 feed.

quantitive data regarding the shift activity of the catalyst under these conditions, two important observations can be made. The first, illustrated in Figure 4.2.5, is that the presence of water vapor in the feed stream enhances shift activity. The second deals with the CO activity. The N_{CO} values remained essentially unchanged in both the water and water free feed. This catalyst is stable to water in the feed stream and the results also suggest that H_2O does not efficiently compete with CO adsorption on the catalyst surface. The data cannot be analyzed quantitatively but do raise an interesting question. Does the shift reaction and FT synthesis occur on the same catalytic site?

The alloy's activity remains stable to small abrupt changes in the water concentration of the gas stream. These results indicate that the catalytic surface is not susceptable to back oxidation by water vapor and that water may not be the cause of the loss in catalytic activity observed in section 4.1. The methanol yield (or production rate) remained unchanged for the two feed conditions. This observation is consistent with the shift reaction and methanol formation reaction occuring over independent catalytic sites. Although similar studies were not performed on the Fe catalyst, experiments involving iron nitride catalyst indicate that warm up of the water trap during on stream operation results in no appreciable loss of either CO or shift activity (128).

4.3 Product Yields of the Low Molecular Weight Products

The yield of product i, Y_i, with respect to reactant j is defined below.

$$Y_i = \frac{\text{moles of } j \text{ converted to } i}{\text{moles of } j \text{ present initially (0\% conversion)}} \qquad 4.3.1$$

All product yields will be given with respect to one mole of feed consisting of either a 1/1 or 1/3 CO/H_2 mixture. In this section the yields are presented as a function of precent CO converted. This permits the direct comparision of a catalyst's ability to produce a given component with respect to the total CO consumed.

4.3.1 Product Yields of Low Molecular Weight Olefins for Fe Catalyst with 1/3 CO/H_2 feed.

The ethylene, propylene and 1-butene yields are shown in figures 4.3.1, 4.3.2, and 4.3.3 respectively. There is a decrease in the ethylene and propylene yields with increasing pressure for a fixed CO conversion level. The 1-butene yield increases over 150% at higher pressures over the conversion range studied. These trends with pressure are due to the overall shift in the hydrocarbon produce distribution towards higher molecular weight products at elevated pressures. The large increase in 1-butene yield at higher pressures is also due to the decrease in isomerization activity with increasing pressure. At one atmosphere approximately 30 to 60% of the total C_4 products exist as cis- and trans-2-butene as compared to less than 10% at 14 atmospheres. The isomerization activity of the catalyst is discussed in Chapter 5.

The propylene (Figure 4.3.2) and 1-butene (4.3.3) yields appear to increase linearly with increasing CO conversion. This implies that a fixed fraction of CO reacts to form these products and their yields are not affected appreciably by secondary reactions such as chain initiation,
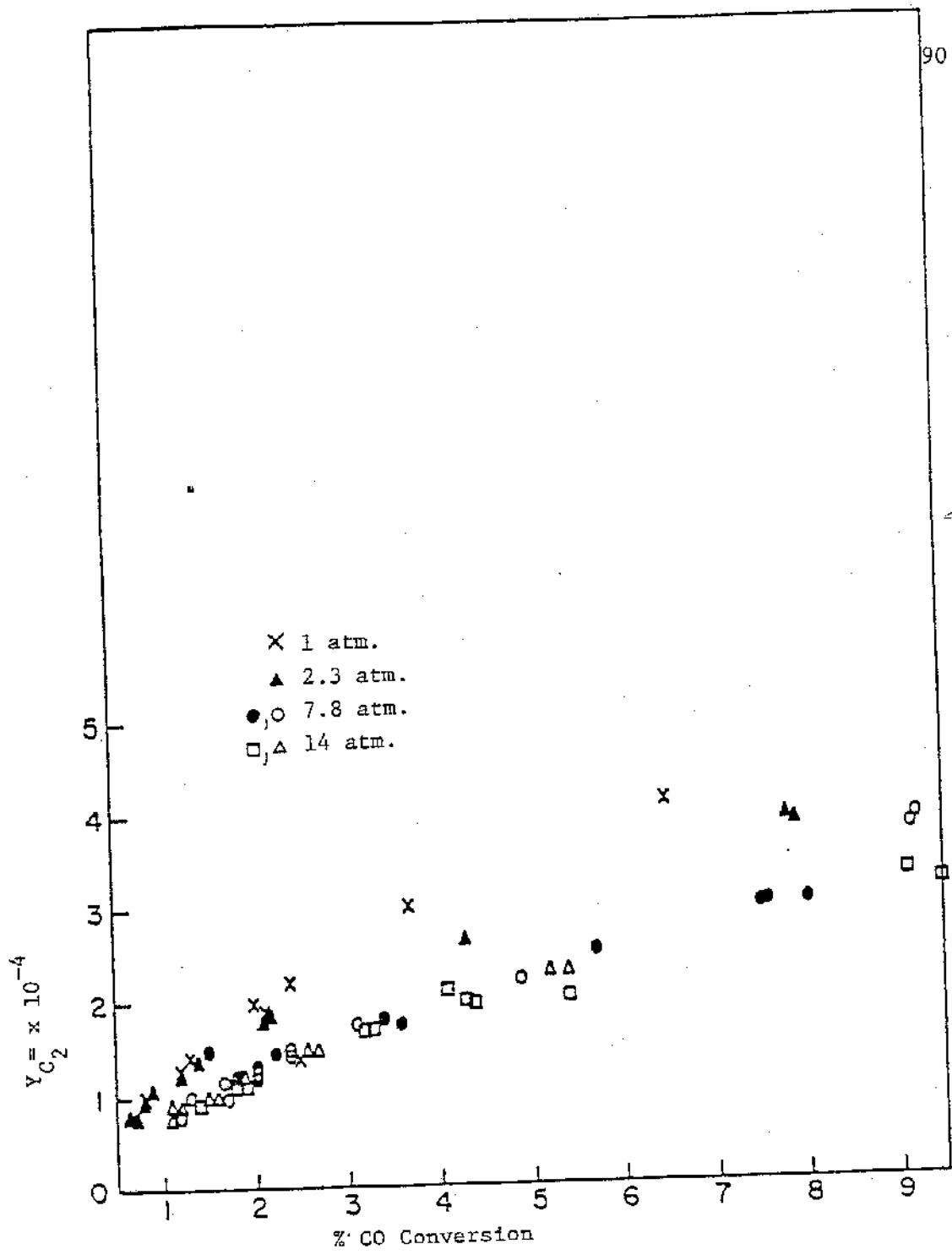
Figure 4.3.1 Ethylene yield versus % CO conversion for the Fe catalyst at 1,7.8 and 14 atmospheres in the 1/3 CO/H$_2$ feed.
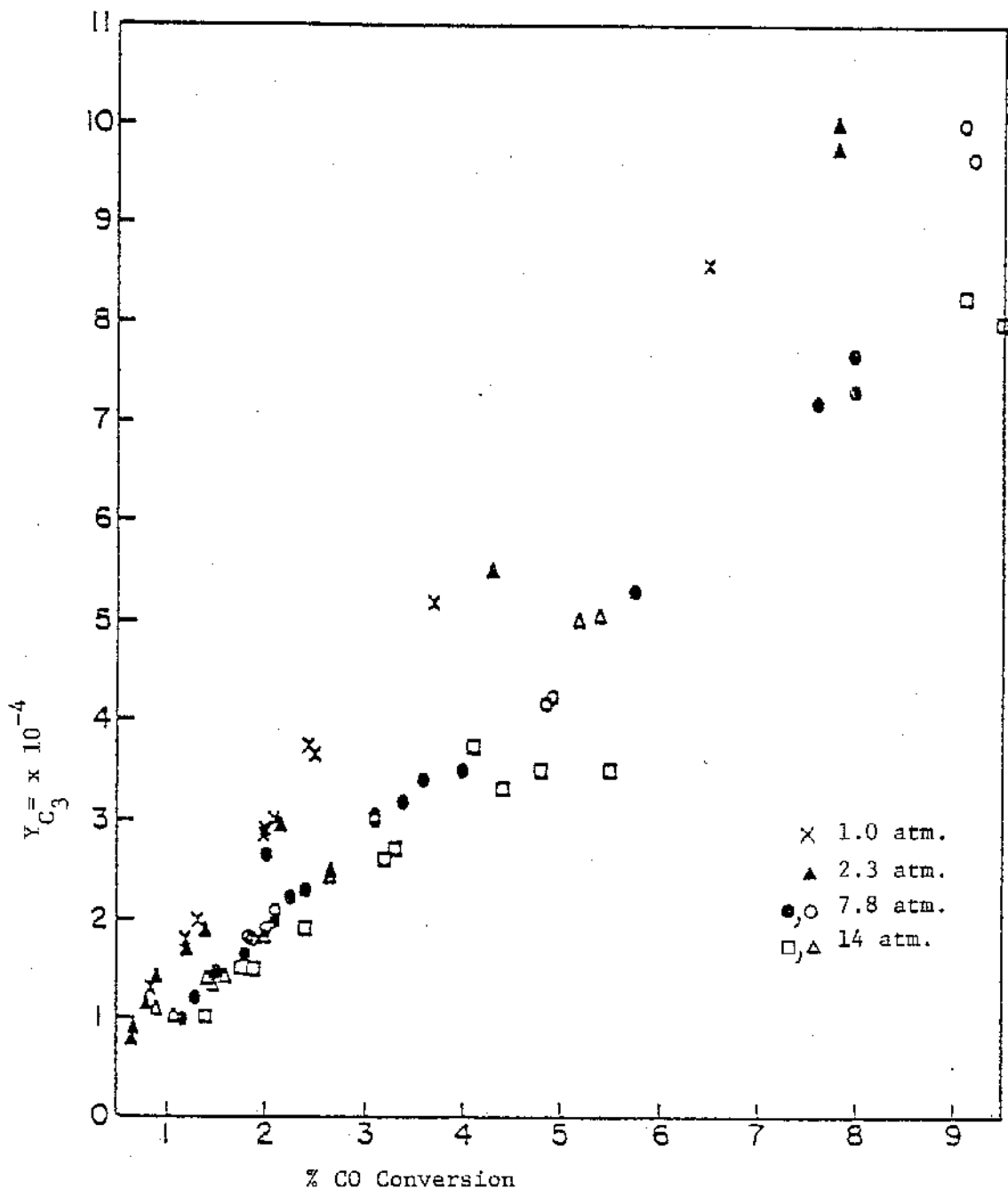
Figure 4.3.2 Propylene yield versus % CO conversion for the Fe
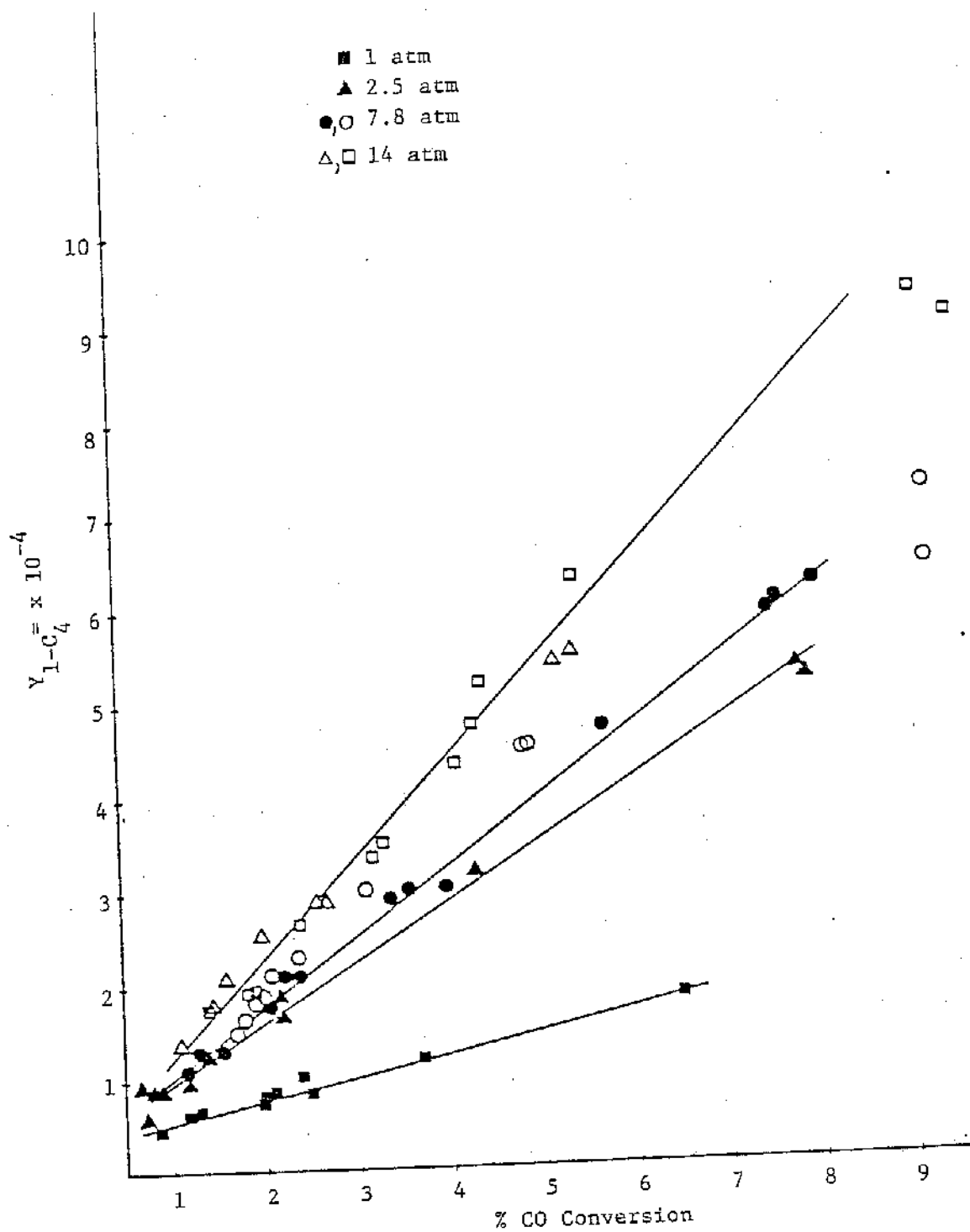catalyst at several total pressures using the 1/3 CO/H_2 mixtures.

Figure 4.3.3 1-butene yield versus % CO conversion for the Fe catalyst at several pressures and 250°C. CO/H_2 feed ratio is 1/3.

hydrogenation or isomerization (1-butene) over the conversion range investigated. In the case of ethylene, the yield (Figure 4.3.1) begins to approach a constant value over the conversion range studied. This behavior is consistent with the fact that ethylene can readily participate in secondary reaction such as hydrogenation and insertion into growing hydrocarbon chains. As discussed in Chapter 2 and 5 this also occurs for the longer chain olefins but to a lesser extent. Most probably, at conversion levels higher than those presented here, the propylene yield would behave in a manner similar to that observed for ethylene.

4.3.2 Olefin/Parafin Selectivity for C_2-C_3 Products for the Fe catalyst
         with the 1/3 CO/H_2 Feed.

In Figure 4.3.4 the olefin to paraffin production rate ratio, $N_{C_i^=}/N_{C_i}$, of the C_2 through C_4 products is plotted against percent CO converted. The $N_{C_2^=}/N_{C_2}$ ratio appears to be relatively independent of pressure, thus there is a corresponding decrease in the ethane yield with increasing pressure. This is an important observation. The ethylene hydrogenation rate changes in a similar manner to the ethylene production rate with increasing pressure. This is suprising in light of the fact that hydrogenation is generally first order in hydrogen partial pressure and zero order in the olefin partial pressure (48). Although it is a well established fact that the Fe catalyst forms a bulk carbide (Chapter 3) and iron surfaces contain carbonacous overlayers at synthesis conditions (Chapter 2), FT investigations have paid little attention to the nature of the active hydrogenation site on the catalytic surface. Most mechanistic studies (82,95,123) implicitly assume that this
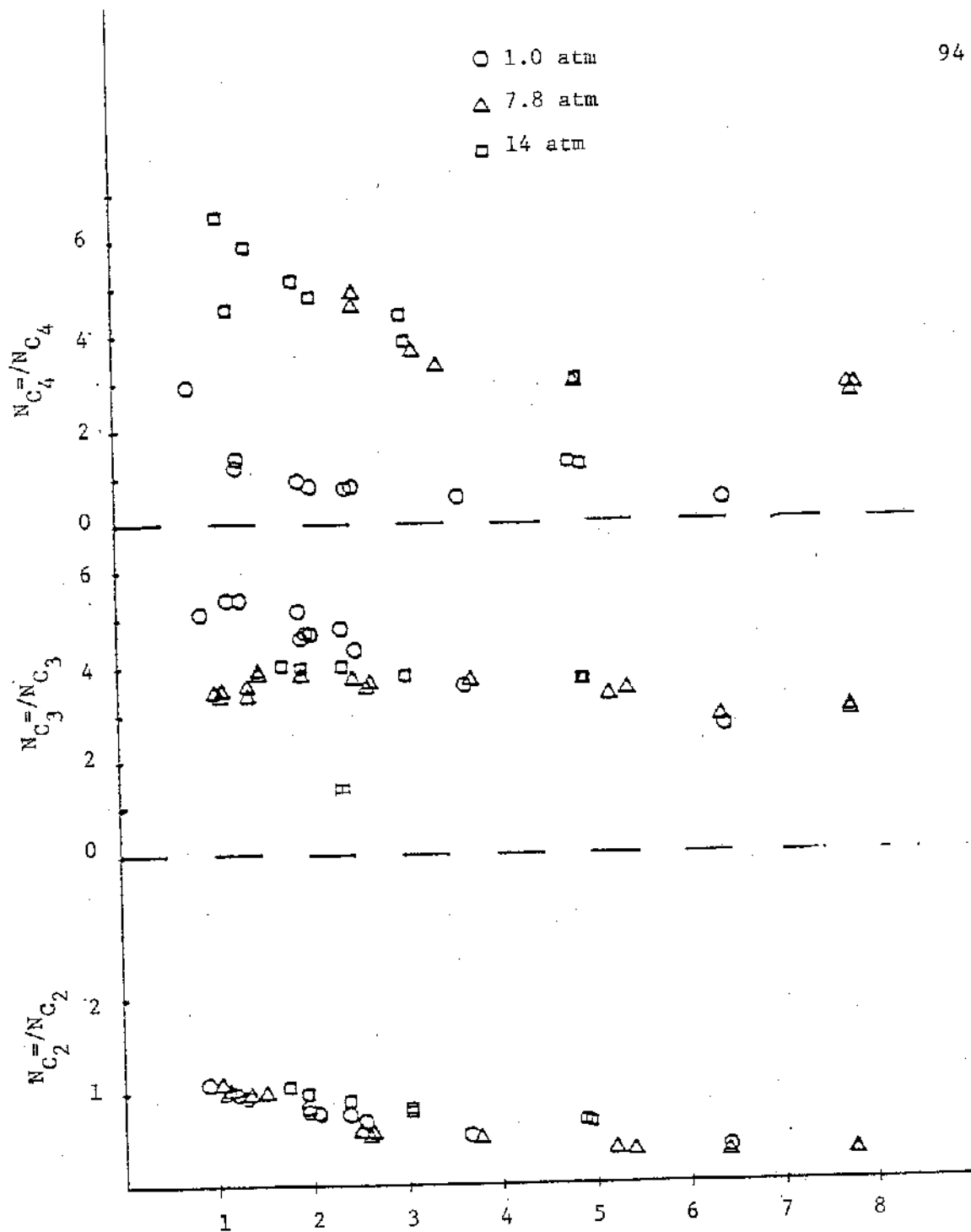
Figure 4.3.4 Ethylene/Ethane (bottom), propylene/propane (middle), and 1-butene/n-butane (top) selectivities versus % CO conversion for the Fe catalyst at 1,7.8 and 14 atmospheres in the 1/3 CO/H$_2$ feed.

secondary reaction occurs on metallic sites formed by the desorption of FT products. This may indeed be the case, however, it is possible that essentially no metallic sites exist on the surface due to the large partial pressure of $CO(26)$. The fact that the ethane yield decreased at higher hydrogen partial pressures suggests that the kinetics of hydrogenation over FT surfaces may not be similar to those of metallic surfaces.

The decrease in $N_{C_2^=}/N_{C_2}$ with increasing conversion most likely represents the combined effects of secondary reactions such as hydrogenation and ethylene initiation of hydrocarbon chains. Similar observations were reported by Amelse et al. (5) and Vannice (123). Secondary reactions involving ethylene are discussed in Chapter 5.

The $N_{C_3^=}/N_{C_3}$ ratio decreases marginally at higher pressures for a fixed CO conversion. The decrease in this ratio with increasing conversion is most pronounced for the alloy catalyst. At higher pressures the ratio remains fairly constant suggesting that the rate of propylene production is comparable to the rate of its consumption through secondary reactions. The $N_{C_4^=}/N_{C_4}$ ratio actually represents the rate of 1-butene production to the production of n-butane and the 2-butenes. The low values of this ratio at one atmosphere are due to the relatively high isomerization activity of the 1-butene to 2 butene reaction at this pressure. The overall olefin to paraffin production ratios for the C_4 products are similar at all pressures studied. This further supports the fact that the hydrogenation rate is not behaving as it should be if it were indeed occurring on a metallic surface.