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### Author

Somorjai, G.A.

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THE FORMATION OF C<sub>1</sub> HYDROCARBONS

G. A. Somorjai

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THE CATALYTIC HYDROGENATION OF CARBON MONOXIDE.  
THE FORMATION OF C<sub>1</sub> HYDROCARBONS

G. A. Somorjai

Lawrence Berkeley Laboratory and Department of Chemistry  
University of California, Berkeley

Abstract

Basic research and development of the catalytic hydrogenation of carbon monoxide has proceeded rapidly in recent years. Using modern surface diagnostic techniques, the atomic level mechanisms of this reaction are being unraveled. It is appropriate to subdivide the processes which occur during the catalytic hydrogenation of carbon monoxide as follows: (1) methanation, (2) methanol formation, (3) polymerization reactions which yield a mixture of high molecular weight hydrocarbons, (4) formation of oxygenated organic molecules, and (5) the insertion of CO molecules (carbonylation) to form C<sub>2</sub> or C<sub>3</sub> products. We would like to know the mechanisms for forming these different products under a variety of experimental conditions. While a complete understanding of the reaction mechanism does not exist, many of the elementary reaction steps and the surface structures and composition of the active catalysts have been verified by careful studies of given catalyst systems. This paper focuses on the kinetics and mechanisms of formation of C<sub>1</sub> hydrocarbons, methane, and methanol. The surface composition of the active catalysts as obtained by electron spectroscopy studies are discussed. The importance of bonding of CO, H<sub>2</sub>, and of the reactions intermediates is emphasized. The role of additives that alter the reaction rates and the mechanism are discussed.

The production of methane and methanol from CO and H<sub>2</sub> are both important processes in chemical technology. They also have a distinguished history as the formation of methane was first reported by Sabatier and Senderens<sup>1</sup> in 1902. Methanol synthesis from CO and H<sub>2</sub> was first reported by Patart<sup>2</sup> in 1921, and in 1923 the Badische Anilin und Soda Fabrik (BASF) announced the synthesis of CH<sub>3</sub>OH to the exclusion of other products.<sup>3</sup> The catalytic reactions that produced these two molecules, however, have been subjected to molecular scale studies only recently. We shall review here what is known about the kinetics and mechanisms of these reactions, about the catalytically active surface, and the nature of the surface chemical bond of CO, H<sub>2</sub>, and the reaction intermediates.

The catalytic studies are pursued in two ways. Dispersed metal particles that are supported by high surface area oxides are used for reaction studies by many. The catalyst configuration and the reactor design are very similar to those used in the chemical technology in this circumstance. Small area ( $\sim 1$  cm<sup>2</sup>) crystal surfaces, films, or polycrystalline foils are used by others. These samples can be well characterized by the various surface science techniques,<sup>4</sup> such as electron spectroscopy (high resolution electron loss spectroscopy, Auger electron spectroscopy, X-ray photoelectron spectroscopy, ultraviolet photoelectron spectroscopy) low energy electron diffraction and ion scattering (ion sputter cleaning, secondary ion mass spectroscopy, and ion scattering spectroscopy). A typical sample configuration used in these model studies is shown in Figure 1. The small area sample can then be inserted in an isolation cell which encloses the sample in a 30 cm<sup>3</sup> volume that is sealed by a copper gasket. The isolation chamber can be pressurized to 100 atm, if desired, and connected to a gas chromatograph that detects the product distribution as a function of time and temperature.<sup>5</sup> The sample may be heated resistively both at high pressure or in ultrahigh vacuum. Such a high pressure isolation cell can be inserted in the middle of an ultrahigh vacuum enclosure, as shown in Figure 2. After the reaction study, the isolation chamber is evacuated and the catalytic surface is analyzed by various surface diagnostic techniques. The reaction at high pressures may be studied in the batch or in the flow mode.

## Methanation

Methane is produced almost exclusively over nickel while it forms along with higher molecular weight hydrocarbons over many other transition metals. Vannice<sup>6</sup> has determined the relative activity of various transition metals for methanation at 1 atm total pressure under conditions in which most other hydrocarbon molecules are not likely to form because of thermodynamic limitations. The order of decreasing activity is ruthenium>iron>nickel>cobalt>rhodium>palladium>platinum and iridium. The activation energy for methanation from CO and H<sub>2</sub> is in the range of 23-25 kcal/mole for ruthenium, iron, nickel, cobalt, and rhodium metals for which this has been determined. The usual temperature range for the catalyzed methanation reaction is 500-700 K, and the turnover frequencies for the more active catalysts vary between 10<sup>-2</sup> to 10 methane molecules per surface site per second. The nearly identical activation energies indicate that the mechanism of methanation is likely to be similar on these various transition metal surfaces. Recent studies in several laboratories clearly show that the dominant mechanism is the dissociation of CO, followed by the dehydrogenation of the surface carbon atoms to methane. The adsorbed oxygen is removed from the surface as CO<sub>2</sub> by reaction with another CO molecule. The net process by which the active surface carbon that is to be hydrogenated forms is often described as the disproportionation of CO (2CO=C+CO<sub>2</sub>) which is also called the Boudouard reaction. This mechanism has been confirmed in several ways. The formation of a carbonaceous overlayer has been detected on polycrystalline rhodium,<sup>7</sup> iron,<sup>8</sup> and nickel surfaces in CO/H<sub>2</sub> mixtures in the temperature range of 500-700 K. After pumping out the reaction mixture and introducing hydrogen, methane is produced at the same rate as in the presence of the CO/H<sub>2</sub> mixtures. Ventrcek et al.<sup>9</sup> and Rabo et al.<sup>10</sup> have been able to titrate the amount of surface carbon by quantitative measurements of the amount of CO<sub>2</sub> evolved over nickel, ruthenium, and cobalt catalysts. After producing the carbon layer by pulses of carbon monoxide, Rabo et al.<sup>10</sup> have introduced pulses of hydrogen to produce predominantly methane. Biloen et al.<sup>11</sup> have deposited the active surface carbon on nickel, cobalt, and ruthenium by dissociating labeled <sup>13</sup>C. The carbon layer is readily hydrogenated subsequently in the presence of a CO/H<sub>2</sub> mixture to yield labeled <sup>13</sup>CH<sub>4</sub>. While Shelef<sup>12</sup> reported the lack of an isotope effect that was expected, if the rehydrogenation of the

surface carbon is the rate-determining step in producing methane, Bell et al.<sup>13</sup> have detected an inverse isotope effect for methanation from ruthenium surfaces; that is, in the presence of deuterium the methanation rate is appreciably higher than in the presence of hydrogen.

While dehydrogenation of the active surface carbon that forms from CO dissociation appears to be the predominant mechanism of methane formation on these transition metal surfaces, it is not the only mechanism which produces methane. Poutsma et al.<sup>14</sup> have detected the formation of CH<sub>4</sub> over palladium surfaces that do not dissociate carbon monoxide. They also observed methane formation over nickel surfaces at 300 K under conditions in which only molecular CO appears to be present on the catalyst surfaces. Vannice<sup>5</sup> also reported the production of methane over platinum, palladium, and iridium surfaces, while independent experiments indicate the absence of CO dissociation over these transition metal catalysts in most cases.<sup>15</sup> It appears that the direct hydrogenation of molecular CO can also occur, but that this reaction has a much lower rate than the methane production via the hydrogenation of the active carbon that is produced from the dissociation of CO in the appropriate temperature range.

Yates and his coworkers<sup>16</sup> have coadsorbed CO and hydrogen at low temperatures (below 150 K) on nickel surfaces. Upon desorption at 200 K, both hydrogen and CO desorbed at the same temperature, indicating a possible reaction intermediate containing both CO and H<sub>2</sub> on the surface. Further studies are essential to determine changes of bonding of CO in the presence of hydrogen that may occur and certainly are indicated by these low temperature studies.

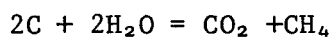
Since the rate of hydrogenation of the surface carbon that deposits upon the dissociation of CO appears to be the rate determining step for methanation, the nature of bonding of this carbon is perhaps the key to the understanding of the methanation mechanism. At low enough temperatures, CO does not seem to dissociate in any other transition metals that are good catalysts for methanation. As the temperature is increased to 300 K and above, CO either desorbs from some of the crystal surfaces of these transition metals or dissociates on others. At present, the mechanism of CO bond breaking is not well understood. There are several binding states of CO that have been well investigated by vibrational

spectroscopy (infrared spectroscopy, high resolution electron loss spectroscopy, and electron tunnel spectroscopy), and by surface crystallography using low energy electron diffraction (LEED).<sup>17,18</sup> On these transition metal surfaces, the intact carbonmonoxide molecule occupies, in general, two types of sites--the on-top and the bridge site. In Figure 3 the electron loss spectrum of CO on the Rh(111) crystal face is shown. The two peaks at high frequencies are associated with the CO stretching frequencies of the molecule in the on-top and the bridge sites, respectively. The low frequency peak is characteristic of the metal-carbon stretching frequency from the CO molecule. At present we do not know which site is most likely to produce dissociative bond breaking of CO under proper experimental conditions of pressure and temperature. On palladium and nickel surfaces, the bridge site is more stable by a few kcal than the on-top site.<sup>19</sup> For platinum and rhodium, the on-top site is more stable by 4 kcal than the bridge site. Figures 4 and 5 show the structure of bridge bonded CO on the Pd(100) surface, and on-top bonded CO on the Ni(100) surface as determined by surface crystallography.<sup>20,21</sup> There is also evidence for the presence of gem-dicarbonyl species on surfaces; that is, species where two CO molecules are bound to each metal atom. However, these are detectable only on dispersed particles of diameters below 100 Å.<sup>22</sup> Since CO dissociation occurs also on single crystal surfaces, where these gem-dicarbonyl species are not usually present, it appears that their presence is not necessary to obtain CO dissociation on transition metal surfaces, although they may provide an additional mechanism for CO dissociation.

The active surface carbon that forms from the dissociation of CO maintains its activity to produce methane only in a rather narrow temperature range. Above 700 K the carbon layer becomes graphitized and loses its reactivity with hydrogen. At temperatures usually below 450 K the dissociation rate of CO to produce the active carbon that is to be rehydrogenated to methane is too slow on most transition metal surfaces to produce the active surface carbon in high enough concentrations. Thus the temperature dependence of the nature of the CO and carbon chemical bonds introduce a narrow range of conditions for the production of methane.



The fact that the dissociation of molecules on surfaces is an activated process is well established by many studies of the formation of surface chemical bonds. Perhaps the most striking evidence for the unique reactivity of the surface carbon that forms in the temperature range of 450-700 K comes from the investigation of Rabo *et al.*<sup>23</sup> It was found that the active carbon that was obtained from CO disproportionation on nickel surfaces reacts readily with water. Upon injecting a pulse of steam at 600 K over a freshly prepared active carbon obtained by the Boudouard reaction, this species rapidly reacted with water to form equimolar CO<sub>2</sub> and CH<sub>4</sub>, according to the following equation:



These experimental results are consistent with the thermodynamics of the reaction between carbon and water. At low temperatures they favor the formation of methane in contrast to the same reaction occurring at high temperatures where the product is CO+H<sub>2</sub>. The carbon surface species on nickel which are deposited in the 450-700 K temperature range are very reactive and react readily with both H<sub>2</sub> and H<sub>2</sub>O, while if these species are aged at higher temperatures they are rendered substantially inert to both.

The reaction of the active carbon with water is also exothermic. This indicates an appreciably weaker bonding of the active carbon over the transition metal than in the case of graphite, since the reaction of graphite with water can be calculated to be endothermic at 600 K by about 3 kcal/mole. The high resolution electron spectrum of the active carbon, after hydrogen adsorption, is shown in Figure 6. The presence of CH species are readily discernible by this sensitive technique. It appears that surface intermediates such as CH and CH<sub>2</sub> are likely to be detectable in future studies of the mechanism of methanation. On nickel surfaces, the formation of C-C bonds among the CH fragments is inhibited apparently due to the outstanding hydrogenolysis (C-C bond breaking) activity of this metal. Thus the direct hydrogenation of C, CH, CH<sub>2</sub>, and CH<sub>3</sub> species results in the rapid formation of methane.

The unique hydrogenation activity of the carbon that forms upon the dissociation of CO on transition metal surfaces in the range of 450-700 K indicates the formation of a reactive multiple carbon-metal bond that deserves further experimental scrutiny. The formation of carbene or carbyne species is not unlikely as these active metal-carbon bonds can yield the

rehydrogenation activity that was detected.

Araki and Ponec<sup>24</sup> have compared the catalytic activity of nickel and nickel-copper alloys for methanation. Upon the addition of less than 10 atm% of copper the activity drastically decreased. Their results indicate that more than one nickel atom is involved in forming a strong and reactive metal-carbon bond that yields methane by direct hydrogenation. Since ethylidyne molecules were detected on the Pt(111) crystal face upon adsorption of  $C_2H_4$  and  $C_2H_2$ , where the strongly bound carbon is in a 3-fold site,<sup>25</sup> a similar location for the carbon or CH fragments on nickel surfaces, which would bind them to three nickel atoms, seems likely. This highly active carbon is metastable with respect to the formation of graphite. Heating to about 700 K produces the stable graphite overlayer that is already active with hydrogen. One of the challenges in developing a stable methanation catalyst is to find additives which inhibit or retard this transformation from active, more energetic and less weakly bound surface carbon to graphite in order to maintain the methanation activity of the transition metal perhaps to higher temperatures.

An interesting change in the kinetics of methanation was observed by Castner *et al.*<sup>25</sup> when the reaction rates were monitored over clean rhodium and oxidized rhodium surfaces in  $CO/H_2$  and  $CO_2/H_2$  gas mixtures. The rates obtained at 600 K, the activation energies, and preexponential factors for methanation are listed in Table I. The turnover frequencies are, by about an order of magnitude, greater on the oxidized surfaces than on the clean metal surface. The activation energies are in the range of 12-15 kcal/mole on the oxidized surface and also when  $CO/H_2$  gas mixtures are used for the reaction instead of  $CO$  and  $H_2$ . This is in contrast with the 24 kcal activation energy for methanation using  $CO/H_2$  mixtures. On the clean metal surface it appears that the oxidized surface is not only a better catalyst, but the mechanism of methanation is very different as indicated by the large change in the kinetic parameters. High resolution electron spectroscopy studies revealed that  $CO_2$  dissociates on the clean rhodium surface to  $CO$  and  $O$ , and thus the molecule may act as an oxidizing agent on the clean metal surface.<sup>26</sup> It is then likely that the  $CO_2$  reaction occurs on a partially oxidized metal surface, and for this reason it exhibits similar kinetics to the  $CO/H_2$  reaction on the oxidized

metal surface.

#### Effect of Alkali Promoters on CO H<sub>2</sub> Reaction

Recent studies have shown the presence of alkali metals on transition metal surfaces, such as nickel, iron, or platinum, change the binding energy as well as the sticking probability of reactive molecules. Bonzel and his coworkers<sup>27</sup> found that the presence of potassium increases the sticking probability of oxygen on platinum and promotes the formation of the oxide on iron crystal surfaces. Also, the presence of this alkali metal decreases the sticking probability of CO on the iron surface and increases its dissociation probability. Madix and Benziger<sup>28</sup> found that the heats of adsorption of both hydrogen and CO increase by the addition of potassium to nickel surfaces. Reactivity studies indicate that the poisoning of iron oxide during the CO/H<sub>2</sub> reaction can be inhibited in the presence of potassium.<sup>29</sup> Potassium seems to inhibit the buildup of graphitic surface carbon that would poison the catalyst by a side reaction that, according to Bell,<sup>30</sup> involves the formation of hydroxides and carbonates of the alkali metals. Recent studies by Ertl<sup>31</sup> indicate that the heats of adsorption of N<sub>2</sub> increase by 3 kcal/mole in the presence of potassium on iron surfaces, and the activation energy for the dissociation of N<sub>2</sub> to nitrogen is decreased by 3 kcal/mole.

It appears that alkali metals markedly change the binding of adsorbates such as CO/H<sub>2</sub> or N<sub>2</sub>. As a result, their relative surface concentration and their dissociation probability will be significantly altered. Thus major changes in reaction rates or reaction mechanisms are expected in the presence of these promoters. Further studies are needed to elucidate the important effects of alkali promoters on transition metals during reactions of these small, but catalytically important, diatomic molecules, CO, H<sub>2</sub>, and N<sub>2</sub>.

#### Methanol Formation

The production of CH<sub>3</sub>OH from carbon monoxide and hydrogen is a commercial process that utilizes a mixture of zinc, copper, and chromium oxides at relatively low pressures (below 100 atm). Recent studies by

Mehta et al.<sup>32</sup> show that interesting changes take place in the catalyst morphology under the reaction conditions. The  $\text{Cu}^{+1}$  ion that is present in the zinc oxide matrix appears to be the active component for methanol production. Chromium appears to increase the solubility of copper in zinc oxide, and the increased  $\text{CO}^{+1}$  concentration leads to higher catalytic activity. There is a great deal of evidence that copper dissolves in zinc oxide and that the solid state reaction is assisted by the presence of  $\text{Cr}^{3+}$  ions. The production of methanol from CO and hydrogen over palladium, platinum, and iridium at high pressures (larger than 100 atm) was reported by Poutsma et al.<sup>14</sup> Palladium appeared to be 10 times more active than platinum or iridium for this reaction. Since these surfaces do not dissociate CO readily, the formation of methanol appears to be the result of the hydrogenation of molecular CO over the transition metals. While similar conclusions can not be reached for the  $\text{CH}_3\text{OH}$  formation over the zinc-copper-chromium oxide catalyst system, in the absence of more detailed studies direct hydrogenation of CO thus provides a reaction channel for the formation of  $\text{CH}_3\text{OH}$ , at least at high pressures.

#### Research for the Near Future

There are several important questions that are raised by recent surface science investigations of the methanation and methanol formation reactions from CO and  $\text{H}_2$ . Perhaps the outstanding question is the mechanism of CO dissociation on the surface. We should like to identify the sites at which CO breaks up to carbon and oxygen. Studies by vibrational spectroscopy could provide the means to obtain such information in the near future. Another important question is the nature of the active carbon-metal bond. By learning the mechanism of its formation, its bonding, its location on the surface, one may be able to make it more reactive, or perhaps stabilize it to higher temperatures against graphitization. Other questions concern the methanation mechanism on oxide surfaces. Oxides are more active, and this beneficial effect should be investigated in more detail. Finally, the promotion or inhibition of C-C bond formation among the C, CH,  $\text{CH}_2$ , and  $\text{CH}_3$  intermediates that form during methanation should be a fruitful area of research.

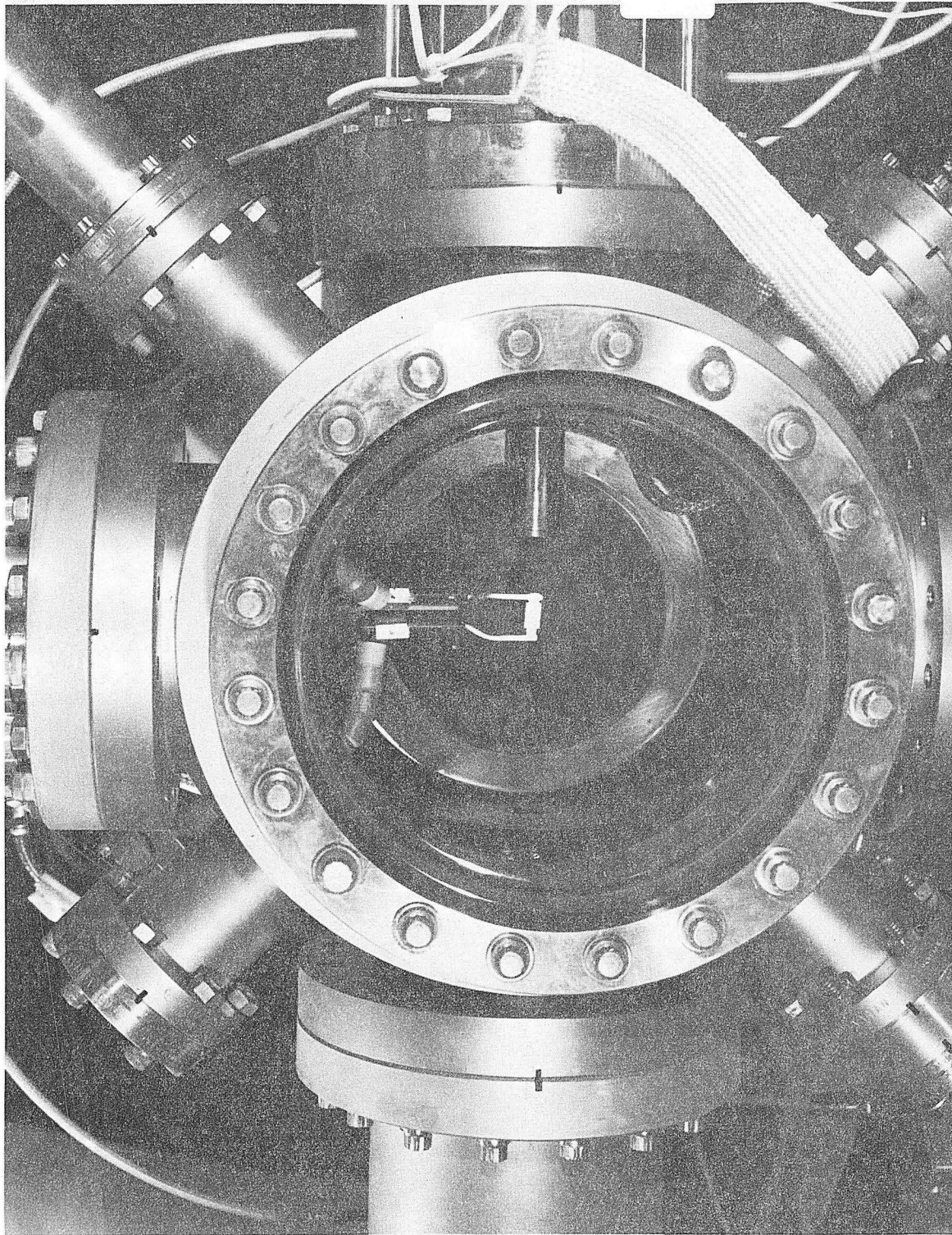
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Figure Captions

- Figure 1. A small surface area sample mounted in a UHV chamber prepared for surface studies.
- Figure 2. High pressure cell built into an ultrahigh vacuum chamber for surface reaction studies.
- Figure 3. Vibrational spectra of CO adsorbed on Rh(111) at 300 K as a function of pressure. These curves were obtained by high resolution electron loss spectroscopy.
- Figure 4. The surface structure of CO on the Pd(100) surface as obtained by surface structure analysis by low energy electron diffraction.
- Figure 5. The surface structure of CO on the Ni(100) surface as determined by surface crystallography.
- Figure 6. CH(CD) species that form on Rh(111) by heating chemisorbed C<sub>2</sub>H<sub>2</sub> or C<sub>2</sub>D<sub>2</sub> to 450 K. These curves were obtained by high resolution electron loss spectroscopy.

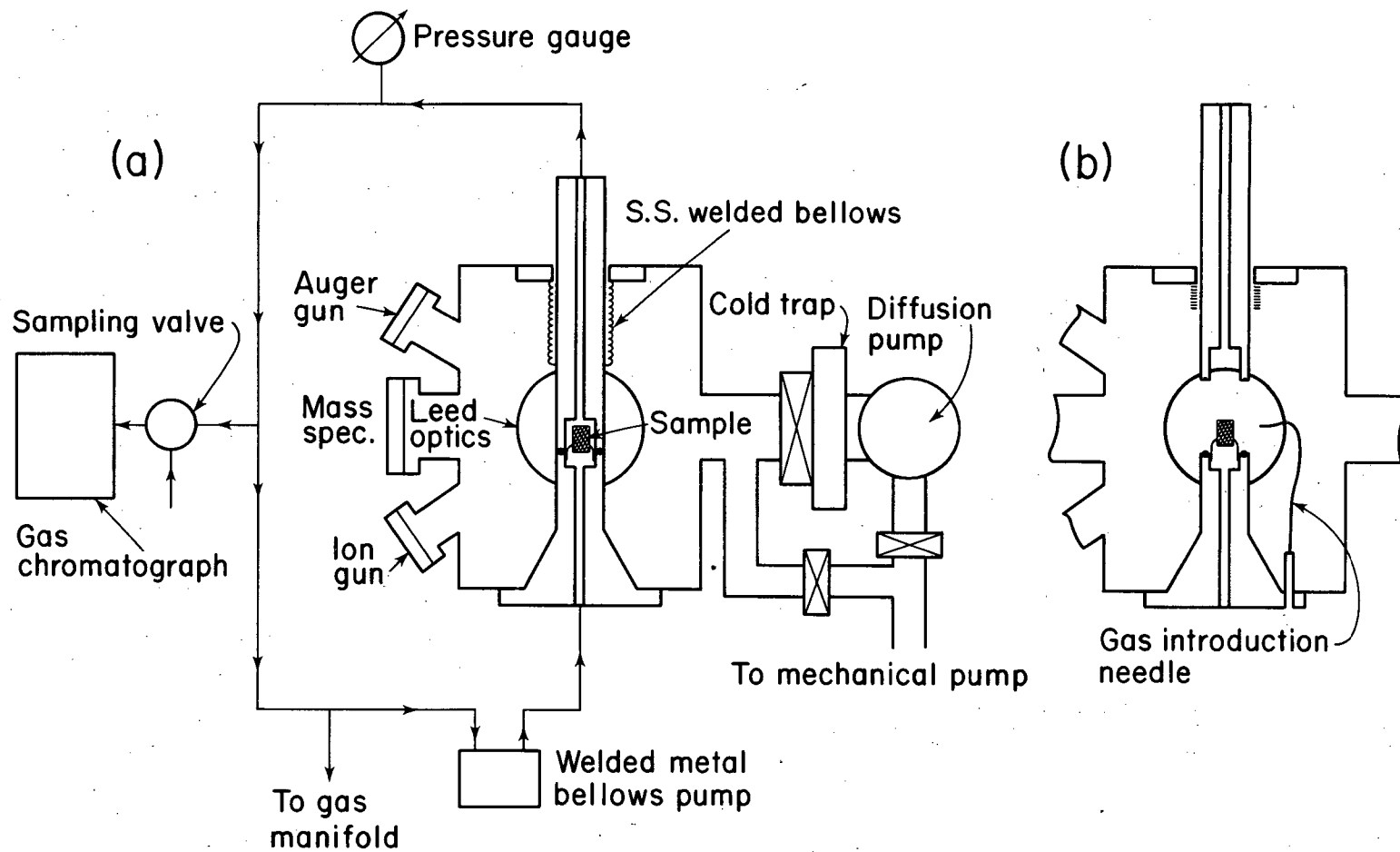


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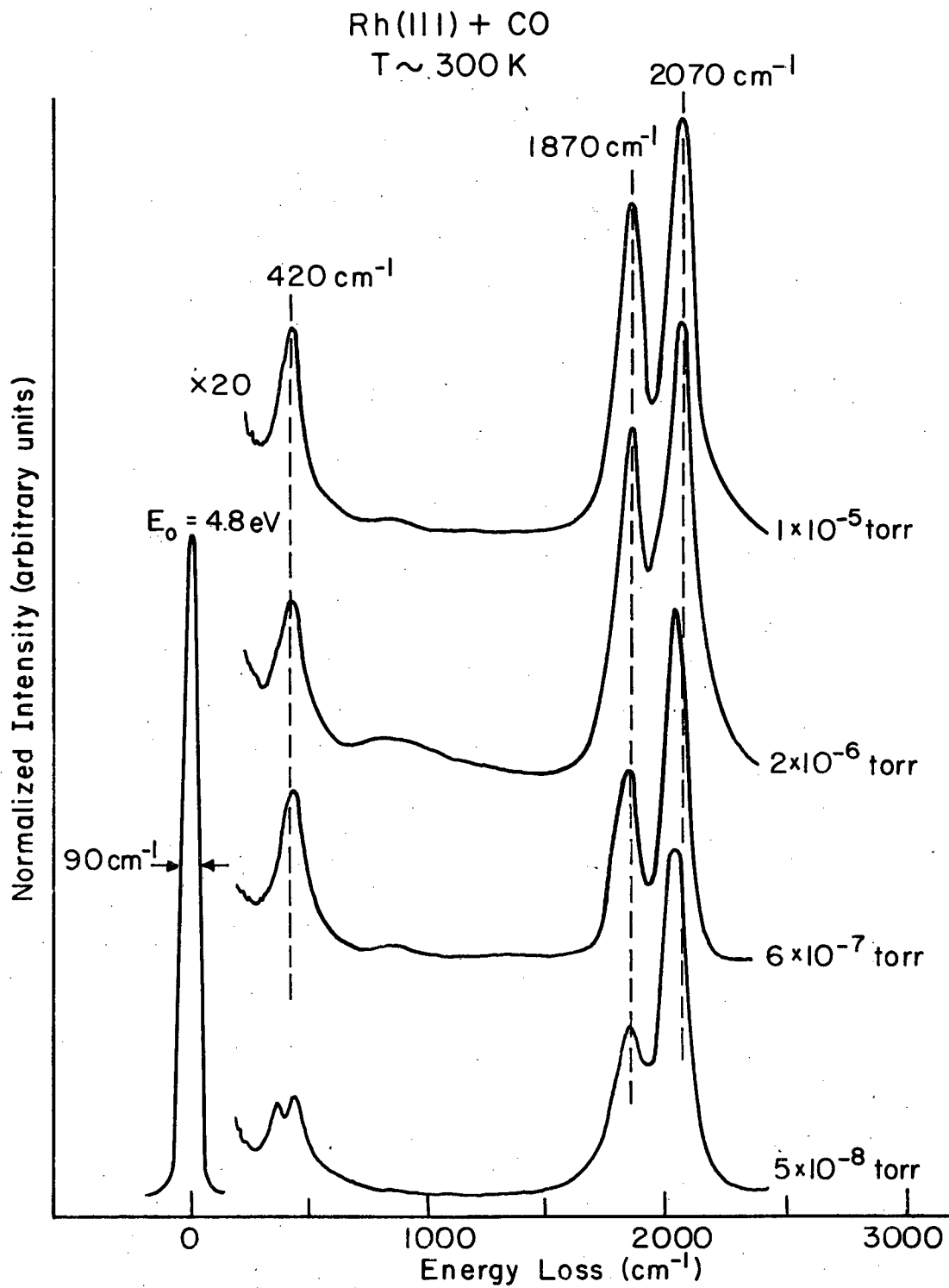
Fig. 1



FIG. 2

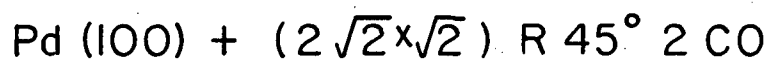
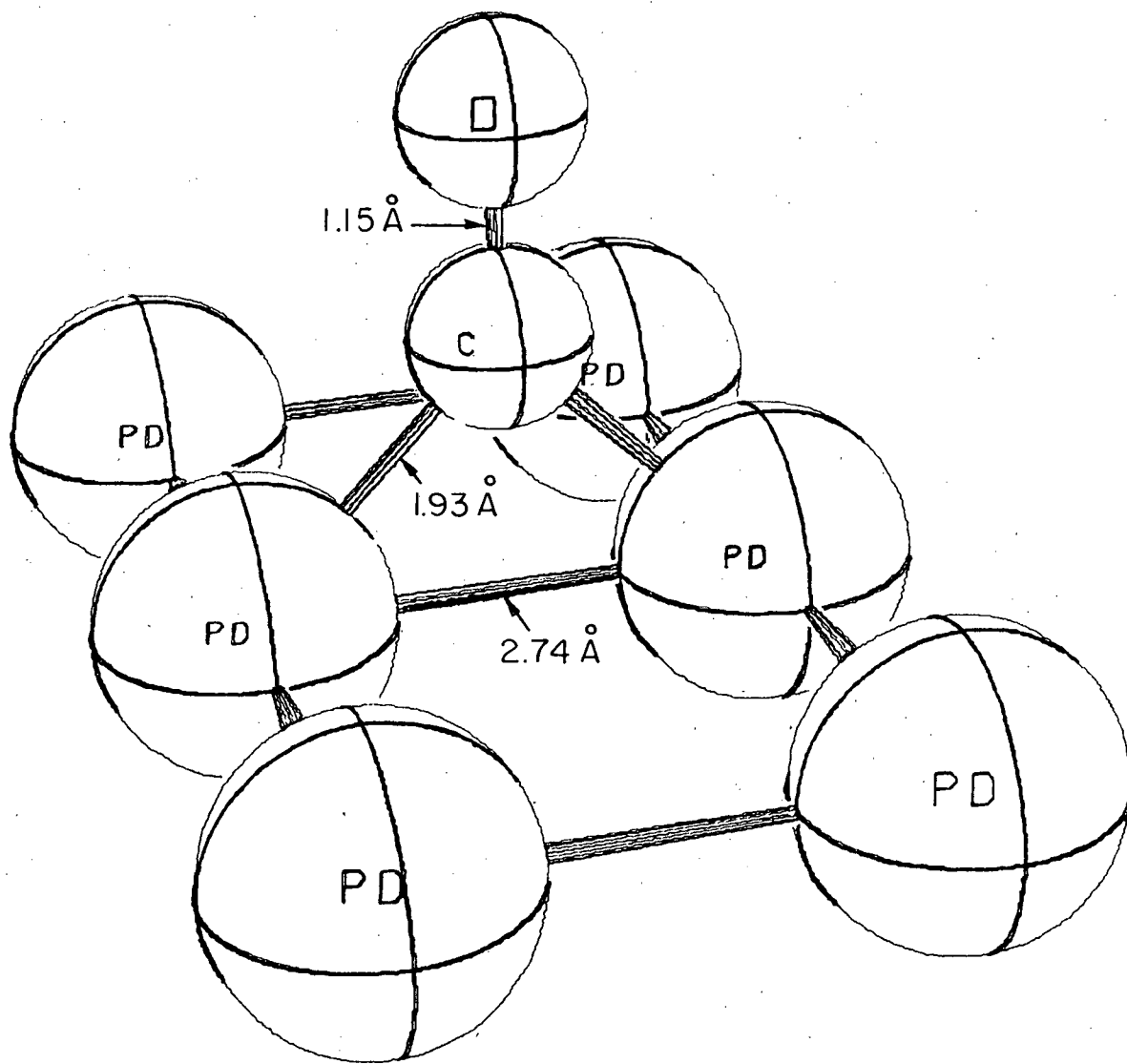


XBL 756-3160



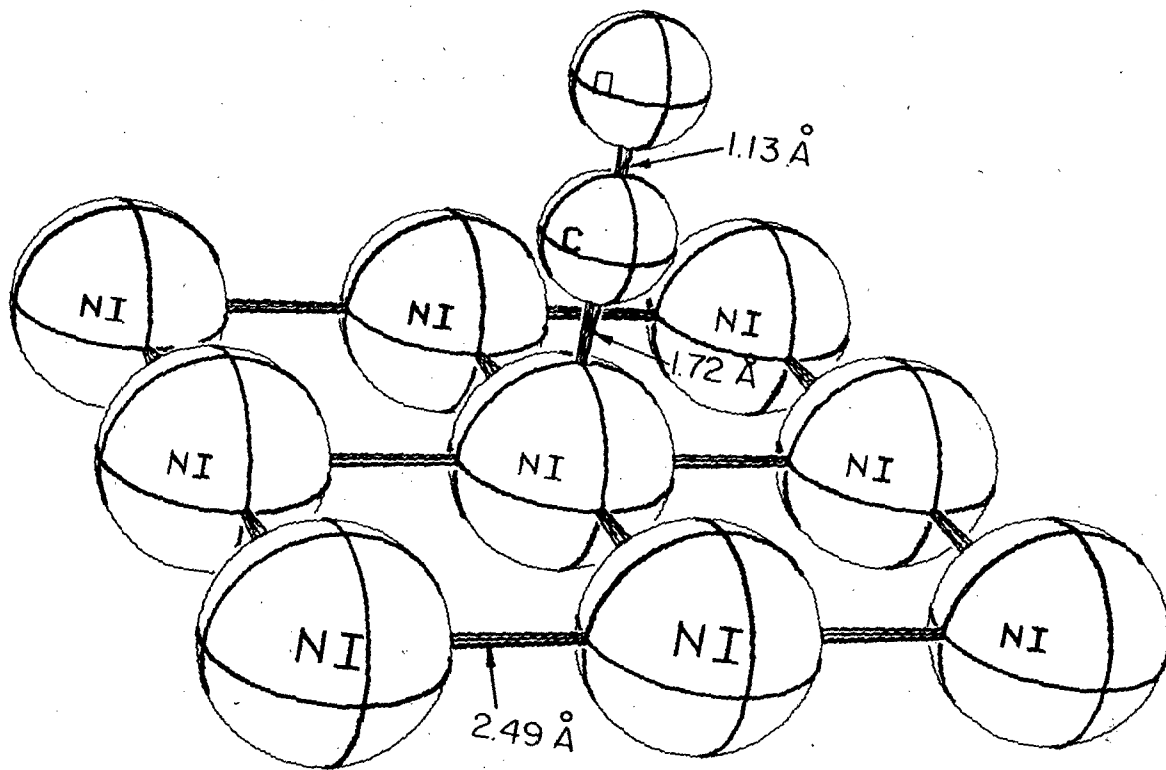
XBL 793-5879

Fig.3



XBL794-6170

Fig.4

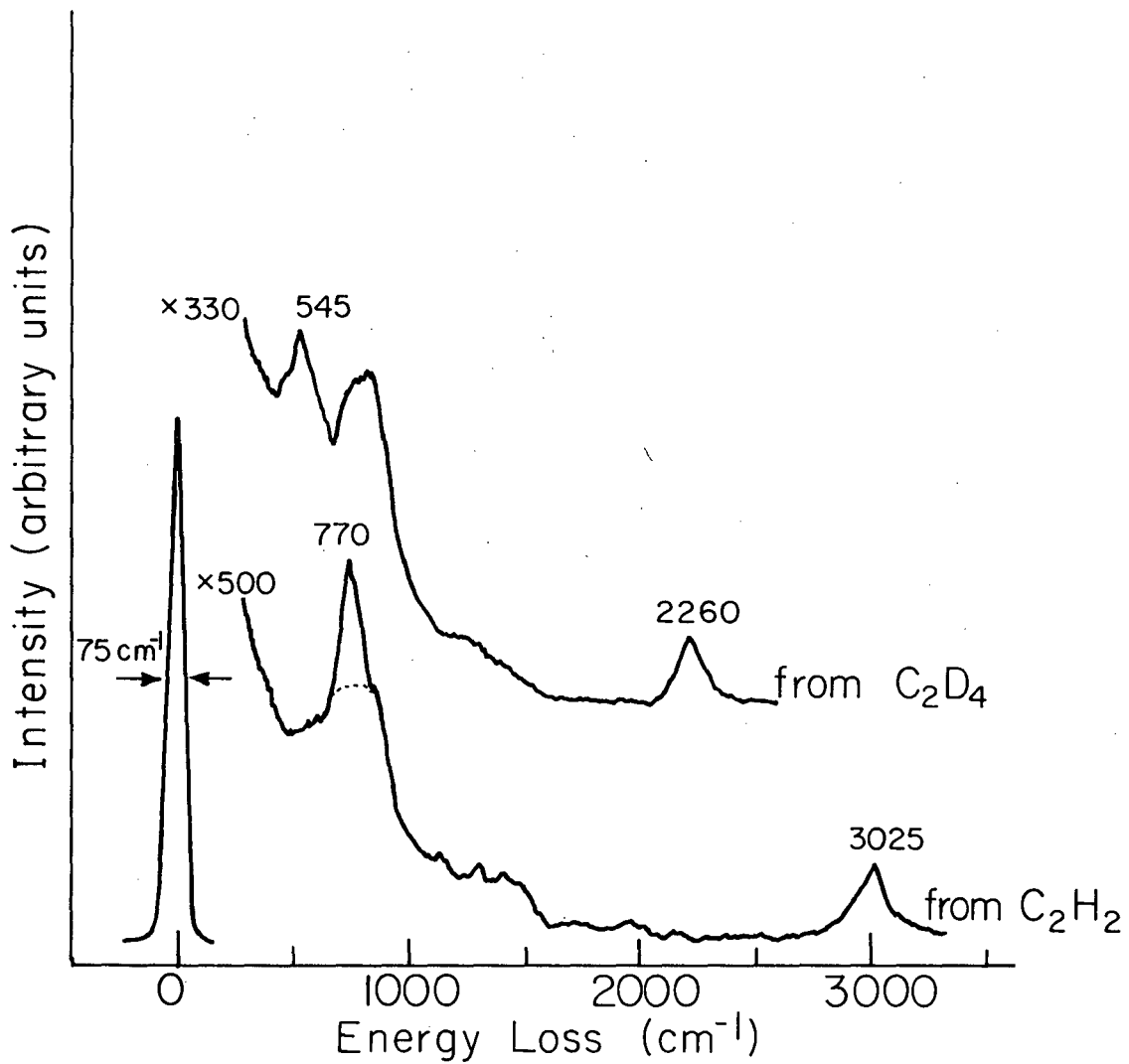


Ni (100) + c (2x2) CO

XBL 794-6169

Fig. 5

CH (CD) Species on Rh (III)



XBL 798-6970

Fig.6

TABLE I. Comparison of the Arrhenius Parameters for Methanation ( $TN + Ae^{-E_a/RT}$ ) for CO and CO<sub>2</sub> Hydrogenation over Polycrystalline Rh Foils.

Reaction Conditions	Surface Pretreatment	Ch <sub>4</sub> TN at 300°C (molec•site <sup>-1</sup> •sec <sup>-1</sup> )	A (molec•site <sup>-1</sup> •sec <sup>-1</sup> )	E <sub>a</sub> (kcal/mole)
0.92 atm, 3H <sub>2</sub> :1CO	Clean	0.13±0.03	10 <sup>8</sup>	24±3
0.92 atm, 3H <sub>2</sub> :1CO <sub>2</sub>	Clean	0.33±0.05	10 <sup>5</sup>	16±2
6 atm, 3H <sub>2</sub> :1CO	Preoxidized	1.7 ± 0.4	10 <sup>5</sup>	12±3

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