FORMATION OF HYDROCARBONS IN THE OUTFLOWS FROM RED GIANTS

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INTRODUCTION

We proposed to study the formation of hydrocarbons in the oxygen-rich outflows from red giants. The existence of organic molecules in such outflows has been known for several years; however, their surprisingly high abundances has been a mystery since all of the carbon had been thought to be irretrievably locked up in CO, the most strongly bound molecule. CO is the first molecule to form from the atoms present in the star's extended atmosphere, and as strong stellar winds drive a cooling outflow, dust grains condense out. In oxygen-rich outflows, the dust is thought to be composed mainly of silicates and other metal oxides. Perhaps the noble metals can condense out in metallic form, in particular the relatively abundant transition metals: iron and nickel. We proposed that perhaps the carbon reservoir held as CO can be accessed through a catalytic process involving the chemisorption of CO and H_2 onto grains rich in metallic iron. CO and H_2 are the two most abundant molecules in circumstellar outflows, and they both are known to dissociate on transition metal surfaces at elevated temperatures, freeing carbon to form organic

molecules such as methane. We believe methane is a precursor molecule to the organics observed in oxygen-rich red giants.

Although the pressures in the circumstellar environment are far lower than those studied in the lab, the temperature range spans that which is favorable for this process to occur, from 450 K up to 650 K and higher. High reactant pressures are preferred in the lab to increase product yield; however, low pressures in nature do not preclude this process from being reasonably efficient because the timescales over which the conditions persist are extremely long. Assumptions of chemical equilibrium are not appropriate for the physical conditions characteristic of outflows, so a kinetic model was required.

When we began this study, the wealth of published experimental data seemed promising, but there had actually been little theoretical modeling done. We needed to develop a chemical kinetic model which reproduced the laboratory experiments in order to apply it to our own temperatures and pressures. We have developed such a model and our results suggest that catalytic methane formation from CO and H_2 is a viable way of accessing the carbon reservoir of CO.

Discussion of Laboratory results - (see figure 1)
I developed the methane formation model based upon results discussed by Sault and Goodman in a review article (a chapter in Advances in Chemical Physics, volume LXXVI "Molecule Surface Interactions"). One set of experiments investigated the rate of carbon buildup on a Ni(100) surface at different temperatures. When a nickel catalyst was exposed to CO, two types of carbon were identified: at T < 650 K, a carbidic (reactive) form of carbon was left behind, and at T > 650 K, the carbon was graphitic (unreactive) in nature. At T < 650 K, this carbidic layer saturated at 0.5 ML (monolayers, where 1 ML is defined as one adsorbed atom per surface atom). The process deemed responsible for both kinds of carbon layers is $2CO \rightarrow C + CO_2(g)$, the Boudouard reaction, also called CO disproportionation. Another significant result of this set of experiments was that the carbon formation rate by CO disproportionation was equivalent to the methane formation rate observed for a H_2/CO mixture.

They concluded from this result that the route to methane wouldn't be slowed down by including a step involving formation of surface carbon, i.e., that the formation of a carbidic layer is fast enough to be a step in the methanation reaction.

Another set of experiments involved pre-carbiding the surface prior to exposure to H_2. Following this step, the carbon removal rate (methane formation rate) was comparable to the carbide formation rate via CO disproportionation, and also to the methane formation rate in a H_2/CO mixture. They concluded that for methane formation in a H_2/CO atmosphere, neither the CO dissociation (carbide formation) nor the subsequent hydrogenation is the rate-limiting step, but rather, there is a delicate balance between the two steps.

Also discussed in the review article was the temperature dependence of the methanation reaction over nickel catalysts. Whether the catalyst was Ni(100), Ni(111), or nickel supported on alumina did not affect the results. From this, they determined that this reaction is structure-insensitive, and found similar results in the catalytic propoerties of other transition metals (Ru and Fe). Arrhenius plots are used to show the relationship in reaction rate as a function of temperature (1/T actually). A plot of log(TON) vs. 1000/T is a straight line for most of the temperature range covered in the experiments. At high T, the line starts to turn over; this is attributed to graphitic (unreactive) carbon forming at T > 650 K or so. The slope of this line is a measure of the overall activation barrier of the process; they got 103 kJ/mole for a total reactant pressure of 120 Torr. I show the experimental line on the plots of my model results.

Legend for figure 1:
All points represent experimental data. Filled circles are for a CO/H_2 ratio (f_{CO}) of 0.25, open circles are for $f_{CO} = 1.0$, and the star-shaped points are three different ratios (0.37, 2.5 and 10). TON stands for turnover number, which is the rate of methane formation in units of molecules per site per second. There are about 10^{15} sites (surface atoms) per cm^3 for nickel. Carbon coverage is denoted by θ_C, and is given in ML (monolayers, where

1 ML corresponds to 1 adsorbed particle for each surface atom). All pressures are given in Torr, 1 Torr = 1333 in cgs units.

Plot B is that chosen by the experimenters to best illustrate the relationship between carbon coverage and TON. All points, regardless of the partial pressures, seem to lie on a smooth curve. Although it is the best correlation, I don't like the implication that θ_C is a function of the TON. A better way to look at this data is to picture the TON and θ_C as functions of the pressure (shown in plots A,C,D,E,F), specifically the H_2 pressure (plots C and E). Both TON and θ_C are well-correlated to $P(H_2)$.

I think that the measured quantities (TON, θ_C) are most closely correlated with the H_2 pressure because the amount of hydrogen on the surface determines how much carbon can be on the surface. CO, when adsorbing all by itself onto the catalyst, will cover the surface with 0.5 ML of C no matter what its pressure might be. Lower pressures will just take longer to reach 0.5 ML, the equilibrium coverage, so there isn't an overly interesting relationship between θ_C and CO pressure. Because CO can be both molecularly adsorbed as a CO molecule, or dissociate into C and O atoms, C is left behind with nowhere to go when CO and O react to form CO_2 (CO disproportionation). This reaction proceeds nicely at temperatures sufficient to dissociate CO. CO can continue to adsorb until θ_C = 0.5 ML. There may be some CO able to adsorb once 0.5 ML of C has been deposited, but the only option it has at that point is to desorb.

If H_2 is adsorbing (putting H atoms on the surface) at the same time CO is, then the H can remove C as methane. O will get removed either as water or CO_2, and as it turns out, it doesn't seem to make a difference in my models whether it is water or CO_2: O will be removed at the same rate as the C is, at equilibrium. I have not found anything definitive in the literature as to whether the O is removed as CO_2 in the presence of hydrogen. Experiments show that more hydrogen (higher H_2 presure) will increase the TON, and they infer that once the H coverage reaches saturation, increasing the H_2 pressure further should not result in a higher TON, but will result in a lower carbon coverage. They also state that under low pressure (and/or higher temperature) conditions where the H coverage is

not saturated, their proposed mechanism must result in a decreasing methane yield and a higher surface carbon concentration. Very high and very low pressures are difficult to achieve in the lab apparently, and a thorough investigation of these extreme pressure regions are not available. However, as I will show, my models demonstrate exactly this type of behavior. In fact, it seems as though the pressure-region investigated in lab experiments is a unique one in that it (barely) spans the region in which the carbon coverage falls from its normal equilibrium value of 0.5 ML to coverages approaching zero.
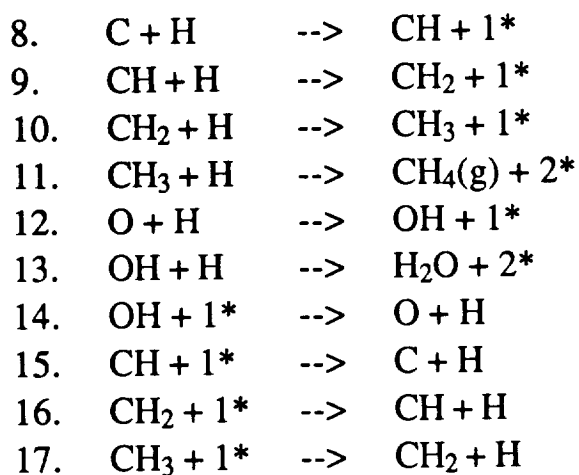
Useful experimental information would include data such as that given in figure 1 for different temperatures, and if possible, a wider range of pressures. That way, we could see what the H_2 pressure is at the point where the TON no longer increases. Once that pressure is known for a certain CO pressure, the CO pressure can be varied to see how it affects the results, if at all. The experiments show that a hydrogen pressure of > 1 Torr is enough to lower the carbon coverage below its normal equilibrium value of 0.5 ML, regardless of what the CO pressure is.

Model description
The model consists of eight differential equations describing the time dependence of the eight surface species involved in the methanation reaction: H, CO, C, O, OH, CH, CH_2, CH_3. There are 17 reactions, or steps, included in this model. Each one is described as a rate term which will show up where necessary in the differential equations.

Table 1. reaction list (* denotes a free site. Unless followed by a (g), all species are adsorbed to the surface.)

1.	$H_2(g) + 2*$	-->	2H
2.	$CO(g) + 1*$	-->	CO
3.	2H	-->	$H_2(g)$
4.	CO	-->	CO(g)
5.	CO + 1*	-->	C + O
6.	C + O	-->	CO(g)
7.	CO + O	-->	$CO_2(g) + 2*$

8.	C + H	-->	CH + 1*
9.	CH + H	-->	CH_2 + 1*
10.	CH_2 + H	-->	CH_3 + 1*
11.	CH_3 + H	-->	CH_4(g) + 2*
12.	O + H	-->	OH + 1*
13.	OH + H	-->	H_2O + 2*
14.	OH + 1*	-->	O + H
15.	CH + 1*	-->	C + H
16.	CH_2 + 1*	-->	CH + H
17.	CH_3 + 1*	-->	CH_2 + H

There are several things to notice about this set of reaction. First, each forward step is balanced by a backward step (the one exception is #6, where C + O go directly into the gas after recombining. This one turns out to be negligibly slow anyhow). Second, there are seven steps which require free sites. At first, I treated all free sites equally, which was a disaster. then I went overboard and treated them all separately. This was a step in the right direction, but as it turns out, it is reasonable to have a unique free-site expression for each species which will inhabit the free site, which means one expression for each of H, CO, and O. It makes good physical sense that this shold be the case, because it should not matter whether the H atom is coming in as H_2, or whether it is coming from a CH dissociating. If the H will occupy a site, it should not really matter what the process is that put it there. The three types of free sites are each a specific function of the coverage of all other species on the surface.

Now, the rate terms must be constructed. Normally, gas phase rate terms of two molecules looks like abundance x abundance x collision rate x Boltzmann factor ($e^{-E/kT}$) where E is an activation energy. The overall rate of the reaction is determined by the slowest step. This is somewhat the case in surface chemistry. The rate terms have the abundance x abundance part (whether the abudance is a free site or another adsorbed particle makes no difference), and also the Boltzmann factor, and the collision rate (or a non-temperature-dependent part, in general) is replaced by a frequency factor, which nominally is the fundamental frequency of lattice vibration, for a particular kind of adsorbate. These values are exceedingly difficult to

measure in the lab, and the slightest variation in surface composition tends to alter it for many of the surfaces investigated in the lab experiments. It is true that for nickel, here have been measured values of this, but once you put anything on the surface, let alone a variety of interacting particles, this number goes straight out the window. My rate terms have ultimately become a non-T-dependent factor, the Boltzmann factor, and the product of two abundances. As it turns out, I do not have to stray far away from published values for activation energies for a clean Ni surface, and the measured frequency factors, to get some really good-looking model results that explain three different sets of laboratory measurements.

Measuring activation energies of surface processes is generally done by measuring the overall rate of reaction and constructing an Arrhenius plot. this gives little to no information about what step might be the critical one, if there even is a specific rate-limiting step. Oftentimes, another experiment is carried out that involves similar steps (for example. the CO disproportionation and methanation reactions) and are found to have comparable overall activation energies. Then, the conclusion is drawn that the step they have in common is dissociation of CO, and therefore the dissociation energy of CO is the rate-limiting step, with an energy equivalent to the overall activation energy of these two processes.

Once I had settled on a good set of free-site functions, based on observations made in experiments, I could start exploring the parameter space of 15 essentially unknown, unmeasured (at least, not directly) activation energies and frequency factors. We came across a paper (Paredes Olivera et al, Surface Science 1995) which had calculated activation energies for the individual steps I was using, but for a clean surface. It seemed like a good place to start, and wound up making all the difference. I started with those values, and an initial guess of 10^{13} for the frequency factors, and worked my way through parameter space using the lab results discussed above a a guide.

Model results

The first set of experiments I attemped to fit were the data for turnover number and carbon coverage as a function of H_2 pressure, which were given for one temperature (T = 625 K). (See figures 2 and 3, which include both my results and the experimental data.) I started with this rather than with the Arrhenius plots because in changing the relative rates of the steps, it makes no difference at all whether I speed up a step by lowering the activation barrier or by increasing the frequency factor. When you're looking at a range of temperatures, this does make a difference. Once I got a respectable looking result, I ran it through a range of temperatures. Then I could fine-tune it by changing the activation barriers of critical steps, and making a compensating change in the corresponding frequency factors to keep the original result for T = 625 K.

Figure 2 shows how the carbon coverage and TON change with $P(H_2)$. The experiments only cover a range of pressures from about 1 torr to 1000 torr. It doesn't seem to matter what the CO/H_2 ratio is (ie, the CO partial pressure doesn't factor in too much, for reasons mentioned above) in either the experiments or in the model results. At low pressures, C will dominate the surface because there is not enough H to remove the C. At high pressures, there is sufficient H to remove almost all of the carbon. In the lab, the C seemed to level off to 0.1 ML, but I believe hat if they had gone to higher pressures, the C-coverage would approach zero, as the model indicates. This does not result in the TON dropping off at high pressures of hydrogen. Instead, it prevents the TON from getting any higher as pressures increase.

One thing to notice with my results is that there is a delay between the C dropping off and the TON leveling off, compared to the experiments. I couldn't get this effect to go away, and I really don't have a good explanation for it. but I was reluctant to just throw the model away because the observed C-coverage behavior is right there, just shifted to higher pressures. It could be due to an experimental effect that I don't know of and/or don't understand.

In figure 3, I show that the C-coverage can be fitted with only a small adjustment in frequency factors. However, the good match with TON

(which I feel is the more critical thing to fit) is lost. I'd rather have the C-coverage off by a factor of 4 or so than the TON off by an order of magnitude.

CONCLUSIONS

We have developed the first non-equilibrium numerical model of a surface chemical (catalytic) process. To construct this model, some very basic equations of surface chemistry needed to be derived and all of the critical steps needed to be included in a physically meaningful manner. We have made no assumptions beyond those required where theoretical and experimental data was not available.

Based on this model, we believe that methane can be formed under the conditions present in circumstellar outflows. Although the methane formation rates are exceptionally low under these conditions, over dynamical timescales, a significant amount of CO can be converted to methane and drive organic chemistry further out in the envelope, explaining the presence of organics there.

Because of the unique nature of transition metals to dissociate CO, a variety of organic compounds can be made using these catalysts. In the lab, different reactant concentrations and catalyst structures or compositions can be fine-tuned to give a very exact product composition and yield. However, based on our model for methane formation over a nickel catalyst, we do not expect higher hydrocarbons to be formed in outflows. Our intent in modeling this process with a nickel catalyst (instead of iron) was due to the availability of both experimental data and theoretical values for the activation barriers. Also, the catalytic activity of nickel and iron are quite similar in the product yield as a function of reactant concentration. In addition, the formation of a reactive carbon layer on the catalyst is a step in this process both for iron and nickel. However, one major difference between iron and nickel is that nickel tends to form only methane from CO and H_2 whereas iron can yield higher hydrocarbons. We attribute this to the fact that the energy barriers associated with hydrogenating the carbon layer tend to make partially hydrogenated products a rarity on the nickel surface. The calculated energy barriers are not yet available for iron, but we expect that these energy barriers allow "fragments" such as CH and CH_2 to remain on the surface long enough to find one another before they find

another H atom; the energy barriers for combination of fragments is also probably quite high. On iron, these fragments must remain on the surface longer (meaning, they avoid being hydrogenated easily) and also, the energy barriers for their reaction to form higher hydrocarbons must be more easily overcome. Unfortunately, the energy barriers have not been measured nor calculated theoretically for these reactions. At very low pressures, it could be possible that some higher hydrocarbons could form on an iron-rich grain; however, the turnover yields would be exceedingly low. Methane is the predominant hydrocarbon formed by this process and we expect that, under favorable conditions and availability of iron-rich grains, it can serve as the tap into the carbon reservoir initially bound up in CO.
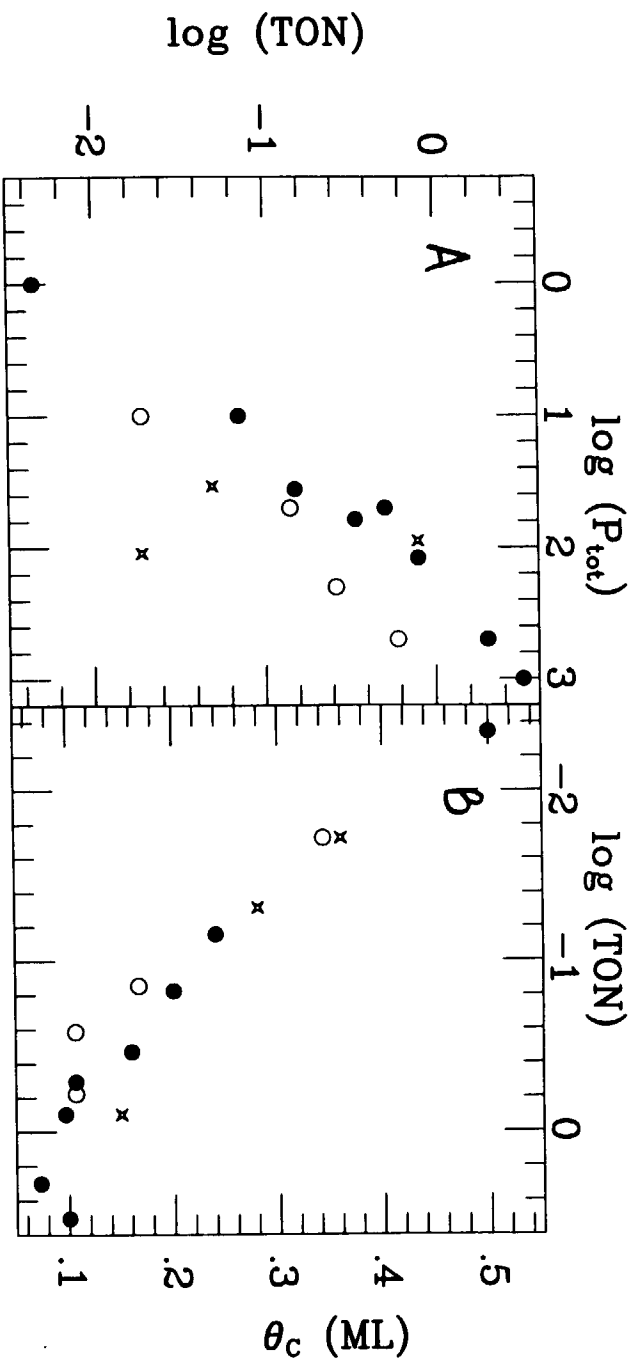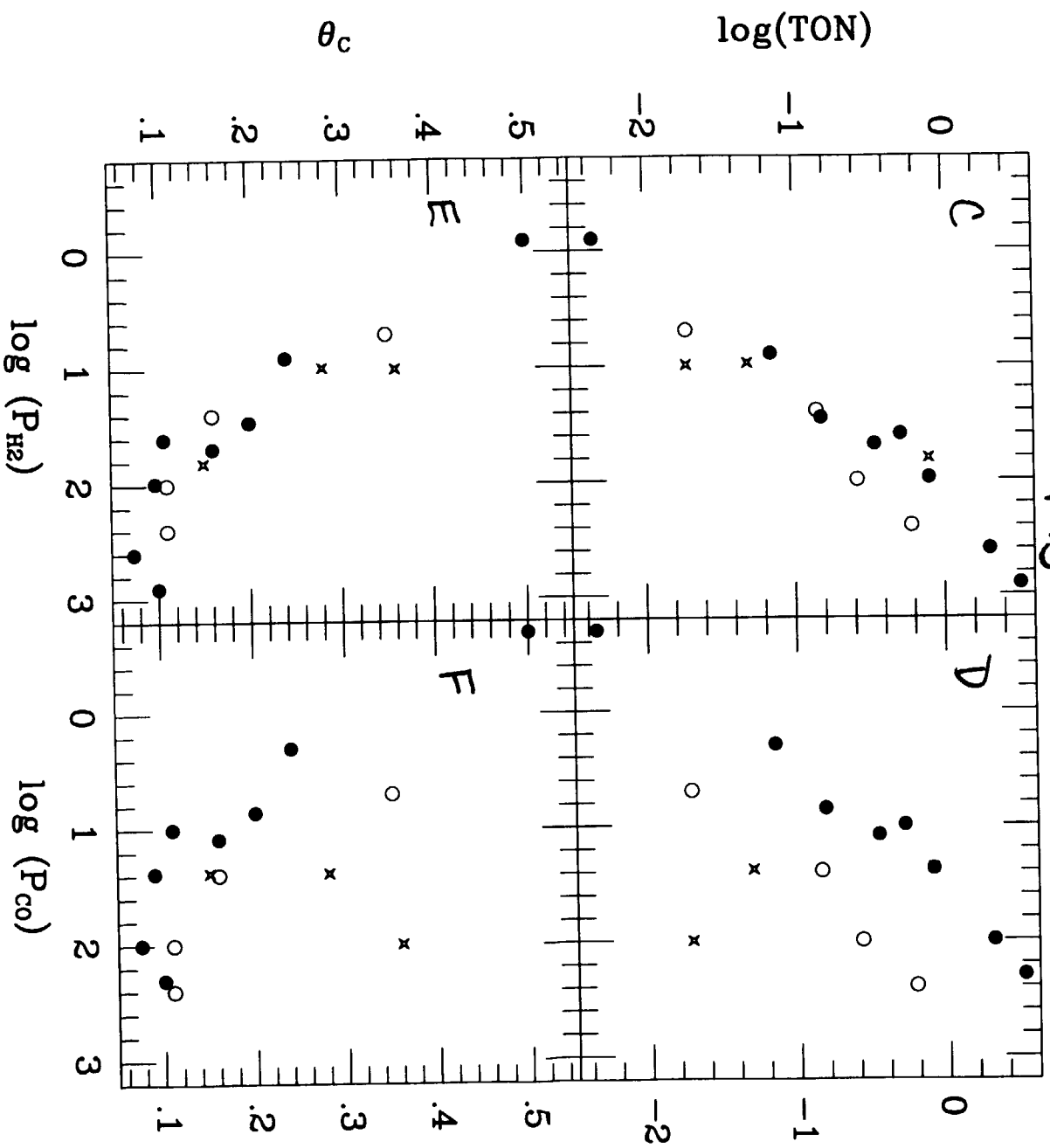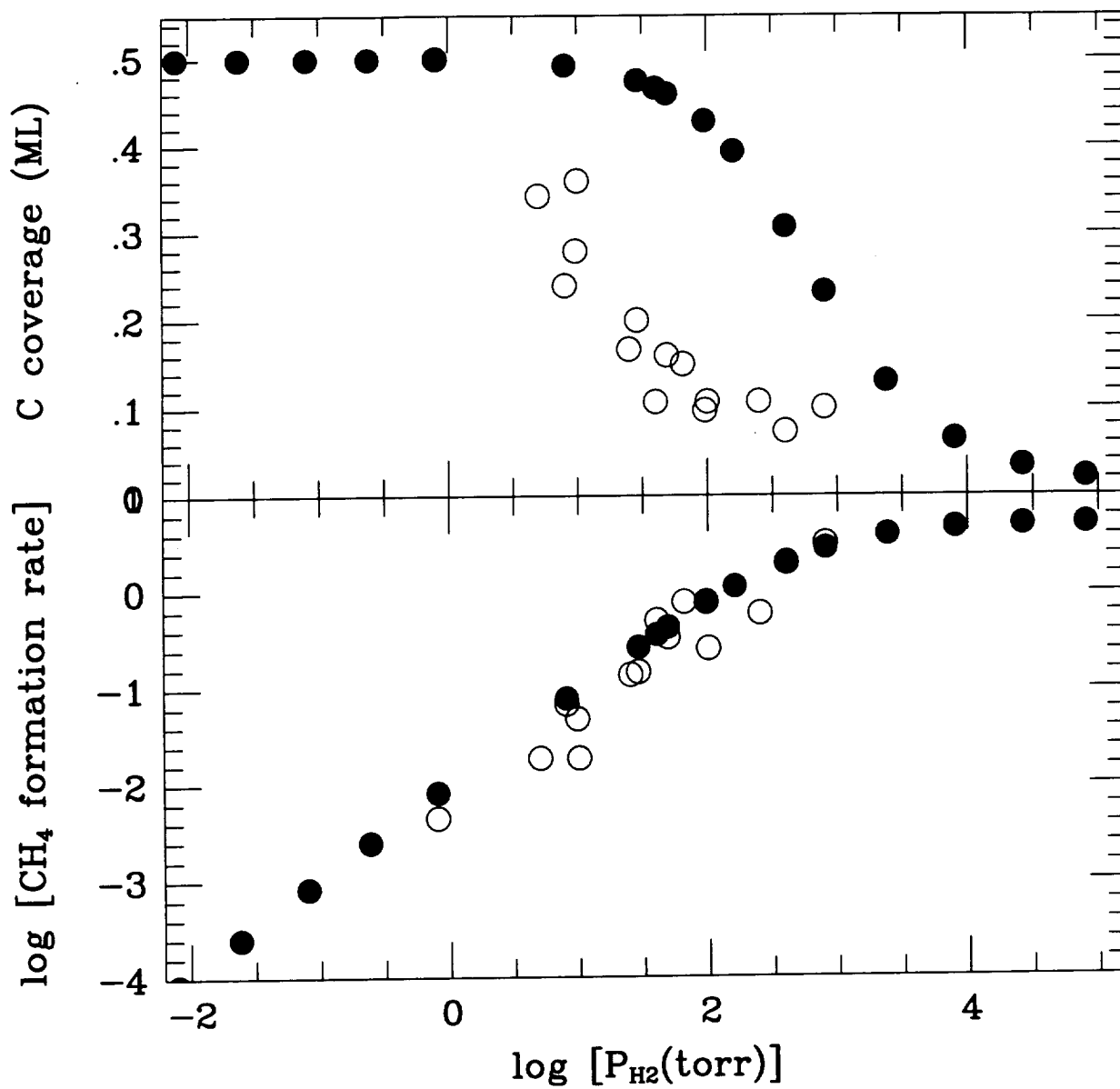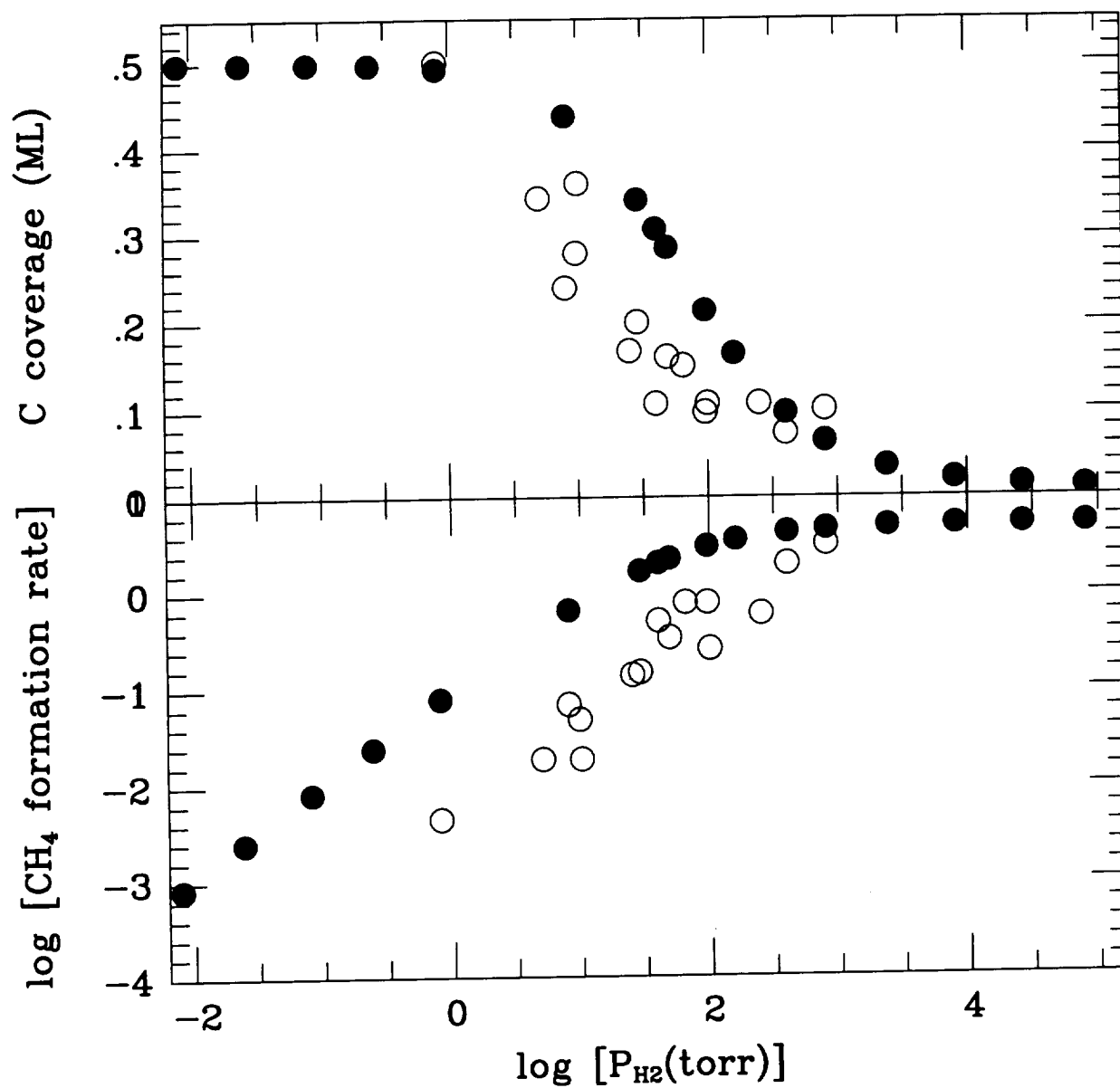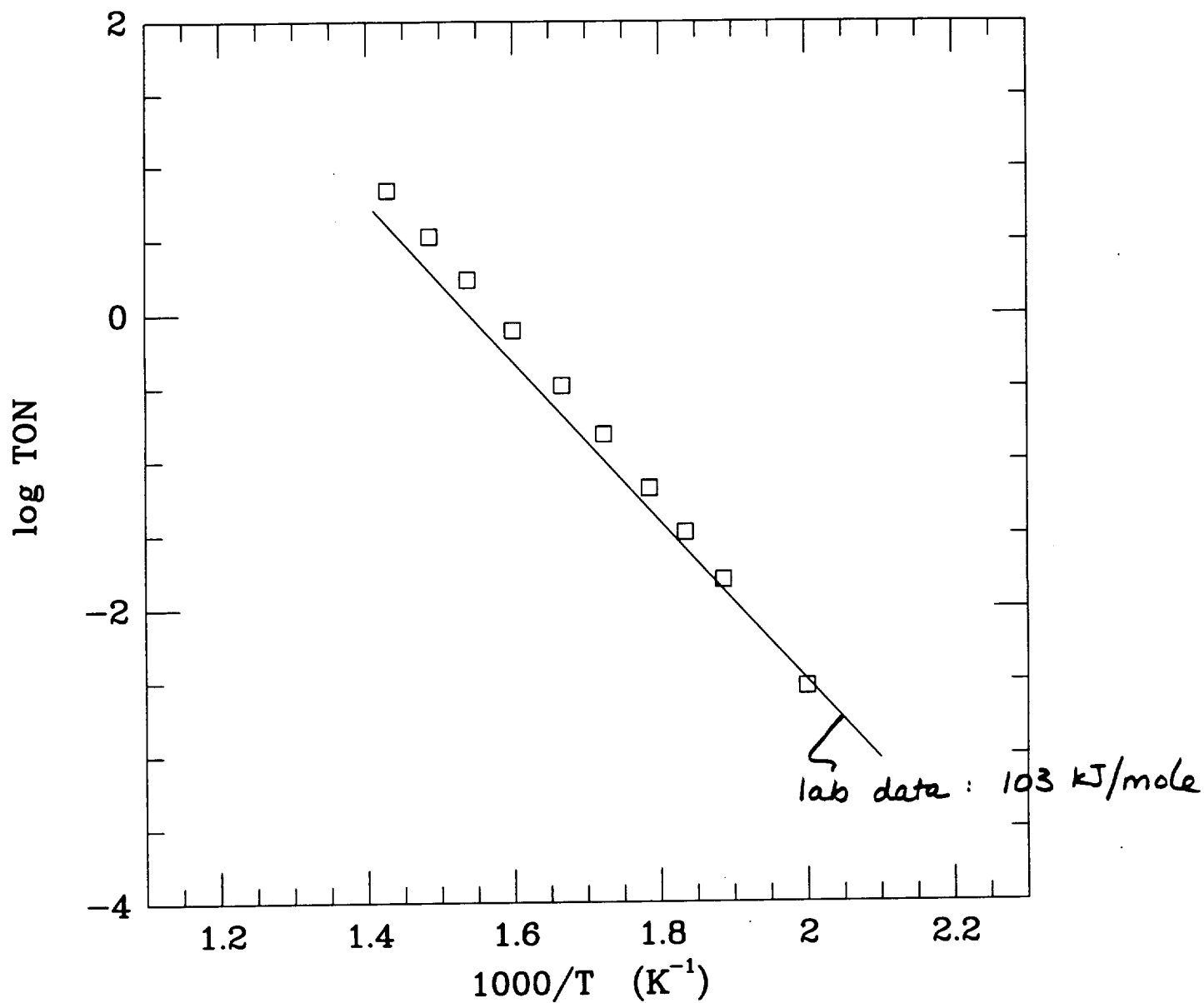
Fig 1.

Fig. 2

T=625 K

Fig.3

T = 625 K

• model Results
o experimental

Fig. 4

$P = 120$ Torr

□   model Result.   111 KJ/mole

――   lab