A CHEMICAL ROUTE TO THE FORMATION OF WATER IN THE CIRCUMSTELLAR ENVELOPES AROUND CARBON-RICH ASYMPTOTIC GIANT BRANCH STARS: FISCHER-TROPSCH CATALYSIS

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ABSTRACT

Fischer-Tropsch catalysis has been suggested as a means of driving hydrocarbon chemistry in oxygen-rich regions such as the protosolar nebula. In addition to producing hydrocarbons, Fischer-Tropsch catalysis also produces water, and it is therefore possible that such processes could account for the recent observations of water in the circumstellar envelope of the carbon-rich asymptotic giant branch star IRC +10216. We present models of the envelope of IRC +10216 and demonstrate that Fischer-Tropsch catalysis on the surfaces of small metallic grains can produce large quantities of water. The abundance of water produced depends on the number density of iron grains that can act as catalysts. If a few percent (0.5%–5%) of the available iron exists as metallic iron or iron/nickel alloy, then Fischer-Tropsch catalysis can produce sufficient gaseous water to account for the observations.

Subject headings: astrochemistry — molecular data — molecular processes — stars: AGB and post-AGB — stars: individual (IRC +10216)

1. INTRODUCTION

The discovery of water in the circumstellar envelope around the carbon-rich asymptotic giant branch (AGB) star IRC +10216 (Melnick et al. 2001) was a surprise since the conditions in the envelope are such that any oxygen present is expected to be contained in CO, leaving little available to form other oxygen-bearing molecules. The observed abundance of water relative to H_2 is $(4–24) \times 10^{-7}$. The presence of water has been explained as being due to the sublimation of water ice from the surfaces of cometary bodies in the circumstellar envelope. These comets would have formed during the main-sequence phase of the life of the star, when conditions were oxygen-rich and water was easy to produce (Ford & Neufeld 2001; Stern, Shull, & Brandt 1990). As the star moved onto the AGB, its luminosity and radius increased, causing any icy bodies close to the star (in a position equivalent to the Kuiper Belt of our Sun) to evaporate. Models estimate this evaporation zone to be about 75 AU. As the star continued to evolve, dredge-up of material enhanced the photospheric carbon/oxygen ratio, resulting in C/O > 1. This is turn altered the C/O ratio in the outflowing gas, so that the envelope would be carbon-rich and normal gas-phase production of water would be inhibited. At this point water vapor could still be produced in the envelope provided that comets existed farther out than the original evaporation zone. As the luminosity of the star increases, the evaporation zone increases and new comets are sublimated, providing a constant new source of water. Ford & Neufeld (2001) modeled this process in IRC +10216 and found that injection of water at $R > 75$ AU at a rate of $(2–4) \times 10^{-10}$ $M_\odot$ yr^{-1} could account for the observations.

Subsequent observations (Ford et al. 2003) have detected OH in IRC +10216, providing further confirmation of the unexpected chemical nature of this source. A fractional abundance of $x(OH) \sim 4 \times 10^{-8}$ was determined, with the OH being formed by the photodissociation of water.

One of the reasons that the cometary scenario was suggested as an explanation of the H_2O observations was the absence of a chemical formation mechanism for this molecule in a carbon-rich environment. However, there is an alternative process that could account for the presen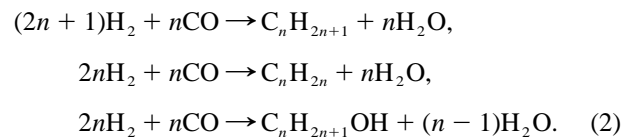ce of H_2O by forming it in situ in the circumstellar envelope. This is Fischer-Tropsch catalysis, the process whereby CO and H_2 are converted into hydrocarbons on an iron or nickel catalyst and water is produced as a by-product. Latter & Charnley (1996) suggested that Fischer-Tropsch catalysis could provide a mechanism to form CH_3OH in IRC +10216 with H_2O also being produced. Fischer-Tropsch catalysis may also have played an important role in oxygen-rich astrophysical environments by breaking up CO and converting the carbon into hydrocarbons. Its possible effects in the protosolar nebula have been investigated by Kress & Tielens (2001) and in oxygen-rich AGB envelopes by Kress (1997). The process can be summarized by

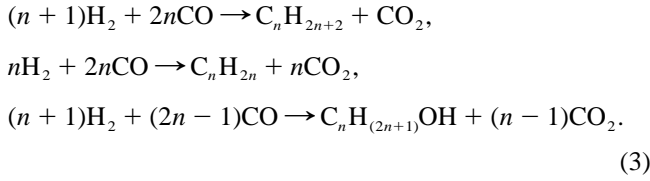$$CO + 3H_2 \Leftrightarrow CH_4 + H_2O. \qquad (1)$$
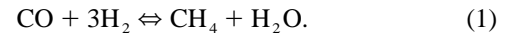
This type of reaction has a high activation energy that prevents their occurrence in the gas phase, but the presence of a transition metal catalyst dramatically lowers the barrier to reaction. If Fischer-Tropsch catalysis can occur in carbon-rich AGB envelopes, then it could provide a means of producing water in these objects. In this Letter we investigate this possibility. We present the results of a simple model of the chemistry of water in a circumstellar envelope that takes into account formation via Fischer-Tropsch catalysis and destruction by photodissociation, and we show that our model can account for the observations of H_2O in IRC +10216.

2. MODEL

Fischer-Tropsch catalysis produces alkanes, alkenes, and alcohols by the processing of CO and H_2 over an iron catalyst by reactions such as

$$(2n + 1)H_2 + nCO \rightarrow C_nH_{2n+1} + nH_2O,$$

$$2nH_2 + nCO \rightarrow C_nH_{2n} + nH_2O,$$

$$2nH_2 + nCO \rightarrow C_nH_{2n+1}OH + (n - 1)H_2O. \qquad (2)$$

A competing set of reactions forms CO_2 rather than H_2O as a by-product:

$$(n + 1)H_2 + 2nCO \rightarrow C_nH_{2n+2} + CO_2,$$

$$nH_2 + 2nCO \rightarrow C_nH_{2n} + nCO_2,$$

$$(n + 1)H_2 + (2n - 1)CO \rightarrow C_nH_{(2n+1)}OH + (n - 1)CO_2. \tag{3}$$

Kress & Tielens (2001) have modeled the experimental data on Fischer-Tropsch catalysis and determined the reaction rates for the formation of CH_4 and C_2H_4 in a form suitable for use in astrochemical modeling. The mechanism for conversion of CO into CH_4 follows a series of steps that are shown in Table 1. These steps have been well established experimentally (Bell 1981; Smorjai 1994). The reactants chemisorb onto the grain surface, with H_2 being dissociated during the adsorption process. CO absorbs as a molecule and only later undergoes dissociation. The surface reactions occur via the Langmuir-Hinschelwood mechanism, i.e., the reactants are first adsorbed onto the grain surface into free surface sites and subsequently react as they encounter each other as they move around the surface. The oxygen produced by CO dissociation rapidly reacts with hydrogen atoms and is returned to the gas as H_2O. The carbon is converted into CH_4, also by sequential hydrogenation. C_2H_4 is produced by the reaction of two CH_2 radicals.

It is important to note that the model of Kress & Tielens (2001) does not include the competing reactions that lead to CO_2 rather than H_2O (eq. [3]). The results presented here therefore represent an upper limit to the water abundance that can be produced as a result of Fischer-Tropsch catalysis in AGB envelopes.

One question that must be addressed before we can begin our model is the nature of the dust grains in a carbon-rich circumstellar envelope. Is there any metallic iron available to act as a catalyst? Equilibrium condensation calculations suggest that iron particles will condense in circumstellar shells irrespective of the C/O ratio (Jones 1990). Iron can condense as metallic iron, iron/nickel alloy, or iron carbide in carbon-rich environments between 2000 and 900 K with the nature of the major iron carrying phase being dependent on the total pressure (Salpeter 1977). In an oxygen-rich circumstellar envelope, iron grains will be oxidized below about 500 K. However, in a carbon-rich envelope, where there is little free oxygen, any metallic iron or iron carbide grains will be more likely to survive without chemical processing (Jones 1990). It is therefore reasonable to assume that at least some of the iron ejected from the star will exist as metallic iron or iron/nickel alloy grains in the circumstellar envelope where they can act as a catalyst for Fischer-Tropsch type reactions.

Estimates of the iron grain abundance in the circumstellar envelope around the oxygen-rich AGB star OH 127.8+0.0 have recently been made by Kemper et al. (2002). They found that iron grains, making up 4% of the total dust mass, were required to account for the observed near-infrared emission. No such studies have been carried out in carbon-rich AGB envelopes, such as are considered here, so we have chosen to treat the abundance of iron grains in the envelope of IRC +10216 as a free parameter. We have assumed an iron grain radius of 10 nm in accordance with Jones (1990) and Chlewicki & Laureijs (1988). It is further assumed that the choice of iron grain size and number density will not affect the outflow dynamics, since

TABLE 1
REACTION SET DESCRIBING THE FISCHER-TROPSCH PROCESS
(KRESS & TIELENS 2001)

Reaction	Reactants $\rightarrow$ Products	E_i (kJ mol^{-1})	ν_i (s^{-1})
1	H_2 (g) + $2 f_1 \rightarrow$ 2 H*	...	...
2	CO (g) + $f_2 \rightarrow$ CO*	...	...
3	2H* $\rightarrow H_2$ (g) + $2 f_1$	96	3.2×10^{13}
4	CO* $\rightarrow$ CO (g) + f_2	109	1.0×10^{13}
5	CO* + $f_5 \rightarrow$ C* + O*	109	1.0×10^{13}
6	C* + O* $\rightarrow$ CO (g) + f_2 + f_5	197	1.0×10^{13}
7	C* + H* $\rightarrow$ CH* + f_1	89	3.0×10^9
8	CH* + H* $\rightarrow CH_2$* + f_1	64	3.2×10^{13}
9	CH_2* + H* $\rightarrow CH_3$ + f_1	92	2.0×10^{11}
10	CH_3* + H* $\rightarrow CH_4$ (g) + f_1 + f_2	55	3.2×10^{13}
11	O* + H* $\rightarrow$ OH* + f_1	82	3.2×10^{13}
12	OH* + H* $\rightarrow H_2O$ (g) + f_1 + f_2	83	3.2×10^{13}
13	OH* + $f_1 \rightarrow$ O* + H*	88	1.0×10^{13}
14	CH* + $f_1 \rightarrow$ C* + H*	99	1.0×10^{14}
15	CH_2* + $f_1 \rightarrow$ CH* + H*	97	1.0×10^{14}
16	CH_3 + $f_1 \rightarrow CH_2$* + H*	100	1.0×10^{14}
17	CH_2* + CH_2* $\rightarrow C_2H_4$ (g) + $2 f_2$	89	3.0×10^{11}
18	C* $\rightarrow$ G*	97	3.0×10^6
19	G* $\rightarrow$ C*	30	1.0×10^{-1}

NOTES.—Surface species are indicated by asterisks. Rates are given in the form $k = \nu_i e^{-E_i/T}$ s^{-1}, where T is the dust temperature in units of kelvins. The sticking coefficient, S_x, for H_2 on iron is 0.05 and for CO it is 1, and adsorption rates are calculated as $S_x \pi a^2 n_g(Fe)v_x$, where v_x is the gas-phase velocity of x and $n_g(Fe)$ is the number density of iron grains. Here f_1, f_2, and f_5 are the free sites required by hydrogen, carbon-bearing species, and oxygen, respectively, on the surfaces of grains. $f_1 = 1 - \Theta_H, f_2 = 0.5 - \Theta_{CO} - \Theta_C - \Theta_{CH} - \Theta_{CH_2} - \Theta_{CH_3}$, and $f_5 = \Theta_O$, where Θ_i is the surface coverage of molecule i. Reactions involving G* represent poisoning of the catalyst by accumulation of carbon. For details of the derivation of the rate coefficients see Kress & Tielens (2001).

these grains make up a small proportion of the total grain population. (No assumptions are made about the size distribution of the rest of the grain population that does not affect the efficiency of Fischer-Tropsch catalysis). Given the density of iron (7.874 g cm^{-3}), we can calculate the mass of each 10 nm grain to be 3.3×10^{-17} g. The number of iron atoms in each grain is $3.3 \times 10^{-17}/56N_A = 3.55 \times 10^5$, where 56 is the atomic weight of iron and N_A is Avogadro's number. If all of the iron is in grains, then from the observed solar abundance of Fe/H = 2.69×10^{-5} (Snow & Witt 1996) we can determine a maximum value of the number density of grains relative to total hydrogen, $n_g(Fe)/n_H = 7.6 \times 10^{-11}$. Given that iron could be in forms other than pure metallic grains, we have run models with values of $n_g(Fe)/n_H$ between 10^{-11} and 10^{-15}.

Our model uses the reaction set of Kress & Tielens (2001) to describe Fischer-Tropsch catalysis (Table 1). In addition to these reactions, we also include photodissociation of CH_4, H_2O, OH, and C_2H_4. Since there are no other chemical formation routes to H_2O in the carbon-rich envelope and since photodissociation is the main route to destroy "parent" molecules, this simplified chemistry should give a good estimate of the abundance of H_2O and its radial distribution. The photodissociation rates are calculated using the method of Nejad & Millar (1987), which takes into account the spherical geometry of the source. Grain adsorption rates for CO and H_2 are given by $S_x \pi a^2 n_g(Fe)v_x n(x)$, where S_x is the sticking coefficient (assumed to be 0.05 for H_2 and 1 for CO on iron grains; Kress & Tielens 2001), a is the iron grain radius ($= 10$ nm), $n_g(Fe)$ is the number density of iron grains, v_x is the gas-phase velocity of species x, and $n(x)$ is the gas-phase abundance of x.

We have used the envelope model of Melnick et al. (2001)

TABLE 2
PEAK CALCULATED ABUNDANCES WITH RESPECT TO H_2
FOR VARIOUS VALUES OF $n_g(Fe)/n_H$

$n_g(Fe)/n_H$	CO	CH_4	H_2O	C_2H_4	OH
1.0 (−11)	6.0 (−4)	7.9 (−6)	1.3 (−5)	5.6 (−6)	5.6 (−6)
1.0 (−12)	6.0 (−4)	8.0 (−7)	1.3 (−6)	5.6 (−7)	5.7 (−7)
1.0 (−13)	6.0 (−4)	8.0 (−8)	1.3 (−7)	5.6 (−8)	5.7 (−8)
1.0 (−14)	6.0 (−4)	8.0 (−9)	1.3 (−8)	5.6 (−9)	5.7 (−9)
1.0 (−15)	6.0 (−4)	8.0 (−10)	1.3 (−9)	5.6 (−10)	5.7 (−10)

NOTE.—The peak abundance of OH is found at $R = 5 \times 10^{17}$ cm; for the others the peak abundance is between $R = 2.4 \times 10^{15}$ and 4×10^{17} cm.

to derive the physical conditions in the envelope. The gas temperature is given by

$$T = 12(9 \times 10^{16}/R)^{0.72} \text{ K}, \quad (4)$$

where R is the radial position in the envelope. A minimum temperature of 10 K is assumed. The dust temperature is

$$T_{dust} = 1300(R/R_i)^{-0.4} \text{ K}, \quad (5)$$

where R_i is the dust shell inner radius, taken to be 2.58×10^{14} cm. The gas density is given by

$$n_H = \frac{3.11 \times 10^7}{R_{15}^2} \frac{\dot{M}}{3 \times 10^{-5} M_\odot \text{ yr}^{-1}} \frac{14.5 \text{ kms}^{-1}}{v}, \quad (6)$$

where R_{15} is $R/10^{15}$, the expansion velocity is

$$v = 14.5\sqrt{1 - 0.95(R_i/R)} \text{ km s}^{-1}, \quad (7)$$

and the mass-loss rate $\dot{M} = 5 \times 10^{-5} M_\odot \text{ yr}^{-1}$. We take the inner radius of our model to be $5R_*$ ($= 3.5 \times 10^{14}$ cm). This is the outer radius of the shock region, as modeled by Willacy & Cherchneff (1998), and we use the results of Willacy & Cherchneff to provide the input abundances for H and H_2 for our current model. The input abundances relative to total hydrogen are H = 0.1, H_2 = 0.45, and CO = 3×10^{-4}. The abundance of CO is based on observations (Huggins et al. 1988) and is lower than that calculated by Willacy & Cherchneff (1998). We calculate the abundance distribution out to 10^{18} cm.

3. RESULTS AND DISCUSSION

We find that Fischer-Tropsch catalysis can produce sufficient gaseous water in the circumstellar envelope to account for the observations with the amount of water formed being dependent on the abundance of the catalyst iron grains. Table 2 gives the peak calculated abundances with respect to H_2 for CH_4, H_2O, OH, and C_2H_4 as a function of the abundance of iron grains ($n_g(Fe)/n_H$). We find that the calculated abundances are directly affected by the mass-loss rate assumed, with a factor of 2 reduction in $\dot{M}$ resulting in a factor of 2 reduction in the calculated abundances. Given that our assumed mass-loss rate is at the high end of that derived for IRC +10216, our results represent an upper limit to the abundance of H_2O formed by Fischer-Tropsch catalysis in the envelope.

The radial abundance distributions for two models with $n_g(Fe)/n_H = 10^{-11}$ and 10^{-12} are plotted in Figure 1. Both models show similar behavior in the change in abundance with radius. The water abundance rises quickly to close to its maximum value by $R \sim 1.6 \times 10^{15}$ cm and remains at this level until photodissociation begins to act at $R > 4 \times 10^{17}$ cm. Similar behavior is seen for CH_4 and C_2H_4. OH is a photodissociation product and peaks at $R = 5 \times 10^{17}$ cm before it too is destroyed by photodissociation.

Melnick et al. (2001) derived a water abundance relative to H_2 in IRC +10216 of $(4–24) \times 10^{-7}$ and suggested that the emission comes from the sublimation of comets at a distance between 10^{15} AU and 4×10^{17} cm (the distance by which the dust temperature has fallen below 100 K ∼ the sublimation temperature of water ice). Our models can produce abundances in agreement with this for $1 \times 10^{13} < n_g(Fe)/n_H < 2 \times 10^{-12}$ over a radius of 2×10^{15} to 4×10^{17} cm.

Ford et al. (2003) found OH/$H_2 \sim 4 \times 10^{-8}$ in IRC +10216. The observed OH line profiles are narrower than expected and are blueshifted with respect to the systemic velocity of IRC +10216. Ford et al. suggest that this is due either to an asymmetric spatial distribution of OH or to masing of the OH lines.

OH is produced in the AGB envelope by the photodissociation of H_2O. For our model with $n_g(Fe)/n_H = 10^{-12}$, we find an H_2O abundance of 1.3×10^{-6} (within the observational range) and a peak value of OH/$H_2 = 5.7 \times 10^{-7}$, a factor of more than 10 higher than that observed. A similar value is calculated by Ford et al. in their photodissociation model. In both cases the abundance of OH is determined by the abun-
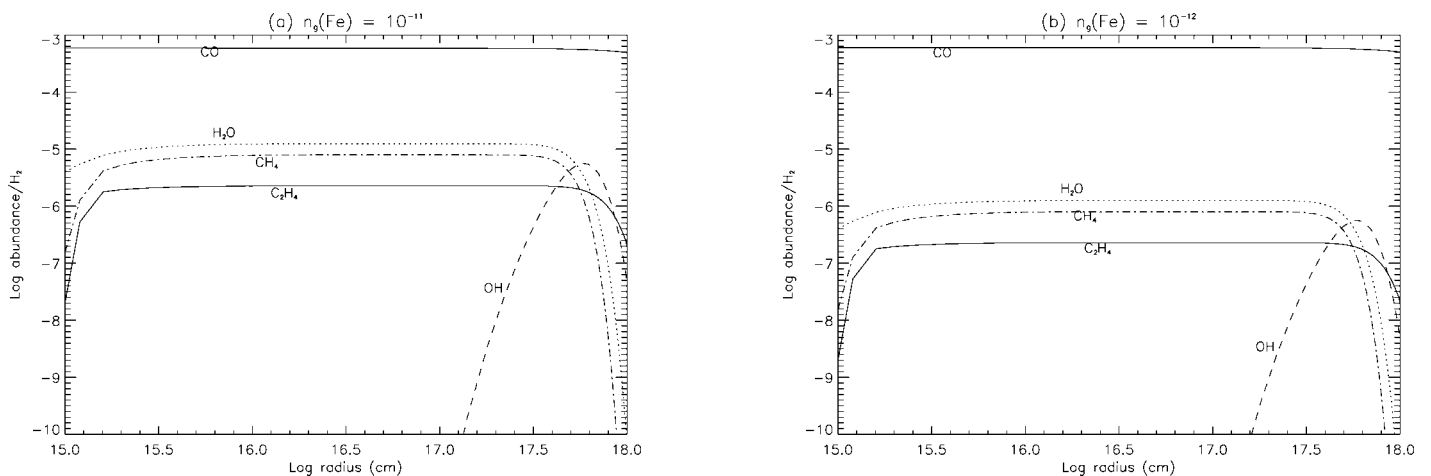

FIG. 1.—Calculated radial abundances with respect to H_2 for (a) $n_g(Fe)/n_H = 10^{-11}$ and (b) $n_g(Fe)/n_H = 10^{-12}$

dance of water assumed to be entering the photodissociation region of the envelope. Given the unusual shape of the OH line, it is clear that more work is required before we understand fully the nature of the OH emission in IRC +10216.

As discussed above, our model does not include the competing set of grain surface reactions that convert CO and H_2 into alkanes, alkenes, and alcohols but that produce CO_2 as a by-product. Our calculated water abundances are therefore an upper limit. However, in view of the low abundance of iron grains required by our model to make substantial abundances of water in the envelope, and that the abundance of water increases linearly with the abundance of iron grains, it seems plausible to assume that even with these competing reactions, H_2O could still be produced easily by Fischer-Tropsch catalysis in the envelope around IRC +10216 if a small fraction of the available iron exists as metallic iron grains.

Recently H_2CO has been observed in IRC +10216 (Ford 2003) with an abundance of $H_2CO/H_2 = 1.1 \times 10^{-8}$. H_2CO is a product of the photodissociation of CH_3OH, which is a po-

tential product of Fischer-Tropsch catalysis (Latter & Charnley 1996). Again, we have not modeled this process explicitly but wish to point out that the presence of H_2CO does not rule out the possibility that Fischer-Tropsch catalysis is important in circumstellar envelopes.

On the basis of our models, we suggest that if 0.5%–5% of iron is contained in metallic iron or iron/nickel alloy grains in the circumstellar envelope, then it is possible to produce water in sufficient quantities to account for the observations without the need to invoke the presence of comets. While this does not prove that comets do not exist in such objects or that they are not the source of at least some of the water detected, it does suggest that the presence of water and of OH in the circumstellar envelope around IRC +10216 is not a sufficient proof of this hypothesis.

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