

## INTERSTELLAR MOLECULES: DIRECT FORMATION ON GRAPHITE GRAINS AT 7-78K

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**Abstract.** The formation of CH<sub>4</sub> and C<sub>2</sub>H<sub>6</sub> by the reaction of H-atoms with graphite when both are at  $T > 7$  K was demonstrated experimentally. In another set of experiments at 78 K, H-atoms produce CH<sub>4</sub> and C<sub>2</sub>H<sub>6</sub>, O-atoms produce CO and CO<sub>2</sub> and S-atoms produce CS<sub>2</sub>. No CN species were formed by N-atoms. Implications to interstellar clouds are discussed.

### 1 Introduction

The theoretical aspects of the recombination of H-atoms on cold grain surfaces has been studied extensively over the years. Apparently, the problem has not been solved completely, as can be seen in recent theoretical studies by Katz et al. (1999) and by Cazaux and Tielens (2004). Three recent experimental studies on recombination of H-atoms to form H<sub>2</sub> molecules were carried out by Pirronello et al. (1999) on amorphous carbon, by Hornekaer et al. (2005) on graphite and amorphous water ice and by Perets et al. (2005) on amorphous water ice. The chemistry on interstellar grains has been reviewed recently by Herbst et al. (2005). Yet, in all the above mentioned studies and in all others, it has not occurred to the authors that H atoms, in addition to recombining on graphite or amorphous carbon, can react with it to form hydrocarbons. Obviously, all the surfaces of graphite

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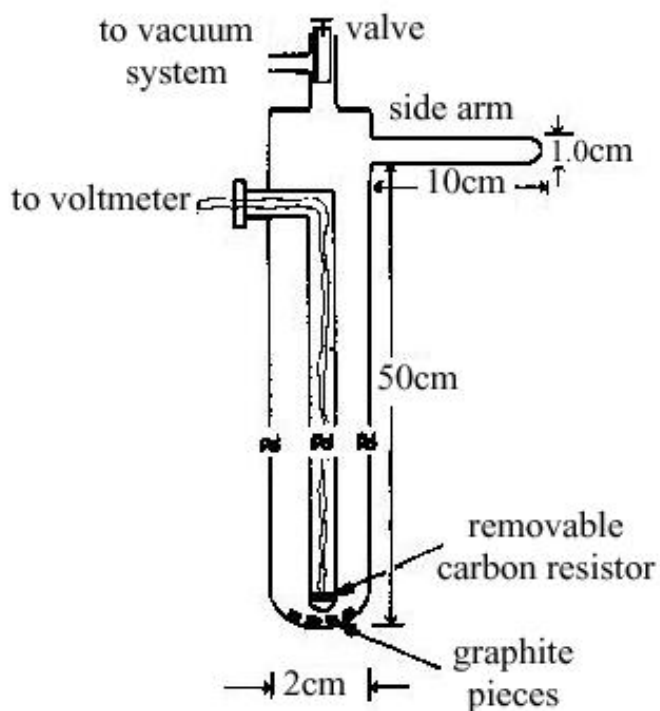
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and amorphous carbon are unsaturated and are prone to reactions with incoming atoms. The reactions of H-atoms with graphite down to 7 K were shown already in 1980 to produce  $\text{CH}_4$  and  $\text{C}_2\text{H}_6$  (Bar-Nun et al. 1980). At 78 K  $\text{CH}_4$  and  $\text{C}_2\text{H}_6$  were produced, as well as CO and  $\text{CO}_2$  with O-atoms and  $\text{CS}_2$  with S-atoms (Bar-Nun 1975). Although no new experimental results became available in the meantime, I would like to draw attention to this mechanism of molecules formation in interstellar clouds and its consequences.

## 2 Experiments with H atoms at 4.6-300K

A detailed description of the experiments is given in Bar-Nun et al. (1980). Therefore, only a brief description is given here. The 50 cm long, 2 cm inside diameter Spectrosil quartz reaction vessel is shown schematically in Fig. 1. For final removal of all remaining traces of organic contaminants, the vessel was filled with pure oxygen and heated to 1200 K, so that the organics would be oxidized to  $\text{CO}_2$  and be removed by pumping to  $8 \times 10^{-6}$  Torr at 1200 K. This burning procedure was performed twice.

In the blank runs, without graphite, either hydrogen (Matheson, Research Purity, 99.9999% pure) or helium (Matheson, Research Purity, 99.9999% pure) were introduced at pressures of 6 Torr into the reaction vessel. A microwave discharge, generated by a 100 W Kiva model MPG-4 microwave power generator, was initiated in the 10 cm long side arm of the reaction vessel. The discharge was visible only in the side arm and did not appear to extend beyond it into the reaction vessel. After 60 min. the discharge was stopped, 200 Torr of either hydrogen or helium was introduced into the vessel and allowed to mix thoroughly with the products for 24 hrs. Analyses of the gas mixture were done on a Packard-Becker model 417 gas chromatograph, using a flame-ionization detector. Pieces of pyrolytic graphite (General Electric, 3 mm long and 0.5 mm thick) were introduced to the bottom of the vessel and pumped to  $8 \times 10^{-6}$  Torr at 1200 K for 2-3 hours. After the vessel was cooled to room temperature, 6 Torr of helium or hydrogen and helium at a pressure of 6 Torr each were introduced. The vessel was then inserted into the neck of a liquid helium dewar. The graphite temperature was monitored by a carbon resistor, (precalibrated by comparison with a germanium cryogenic thermometer) which was inserted into an inner quartz tube filled with helium. After equilibration at the desired temperature, the microwave discharge was switched on in the side arm and



**Fig. 1.** A schematic drawing of the reaction vessel (not drawn to scale)

continued for 60 min. At the onset of the discharge, an increase in temperature of between 0.2-0.4 K was observed. At the end of the experiment, the vessel remained in the dewar for at least 5 min. and then warmed to room temperature, 200 Torr of helium were introduced and the analysis was done 24 hrs. later, to ensure thorough mixing. The experimental conditions and product distribution are presented in Table I.

From Table I, it is clear that  $\text{CH}_4$ , the major product, is still produced by H-atoms impinging on graphite, when both are cooled to 7 K. At 4.6 K, the yield of methane is similar to that of the blank run with hydrogen in the absence of graphite, which suggests that at 4.6 K hydrocarbons are not

**Table 1.** Product Distribution in the Various Experiments

Run	Reactant			Temperature (K)	Products- nmole after 60 min. of discharge			
	H <sub>2</sub>	He	graphite		CH <sub>4</sub>	C <sub>2</sub> H <sub>6</sub>	C <sub>2</sub> H <sub>4</sub>	C <sub>2</sub> H <sub>2</sub>
21	+			300	2.35	---	---	---
22	+	+		300	2.38	0.21	0.21	---
23		+	+	300	0.19	---	---	---
30		+	+	300	0.93	---	---	0.08
32		+	+	300	0.33	---	---	---
45		+	+	300	0.30	---	0.08	---
35	+	+	+	300	10.37	---	---	---
46	+	+	+	78	29.46	0.59	0.22	---
25	+	+	+	20	45.77	0.59	0.09	0.23
37	+	+	+	12	62.20	0.75	0.58	---
38	+	+	+	12	65.65	0.52	0.32	---
44	+	+	+	9	7.62	0.26	---	---
47	+	+	+	9	7.44	0.07	0.52	---
41	+	+	+	7	5.20	---	---	---
42	+	+	+	7	4.60	0.05	0.48	---
40	+	+	+	4.6	1.60	trace	0.27	---

formed. As the temperature is raised, the yield of hydrocarbons increases up to 12 K and then decreases. Two effects are probably responsible for this behavior: at very low temperatures, hydrogen is adsorbed on the graphite until, finally, at 4.6 K no hydrogen is left in the discharge zone. On the other hand, higher hydrogen pressure results in a smaller mean free path for the H-atoms and their subsequent gas phase recombination to form H<sub>2</sub> molecules. The interplay between these two effects may be responsible for the peak in production at 12 K. Because of the adsorption of hydrogen on the graphite, 6 Torr of helium were introduced into the vessel along with the hydrogen, to serve as a heat bath. Although helium is also adsorbed on graphite, it does so to a lesser extent and even at 4.6 K its pressure was higher than 0.5 Torr. This is more than enough to ensure thermalization of the H-atoms through collisions, during their diffusion along the 50 cm path from the discharge to the graphite. Table I also shows that C<sub>2</sub>H<sub>6</sub> at about a 10th of the CH<sub>4</sub> is formed down to 12 K, with some traces of C<sub>2</sub>H<sub>4</sub> and perhaps C<sub>2</sub>H<sub>2</sub> at 20 K. A question might arise as to whether the hydrocarbons could have been formed by trapped H-atoms in the graphite only when the sample was

warmed up to room temperature at the end of the experiment. This is very unlikely, since in our experiments more than 5 min. passed (intentionally) from the time the RF-discharge was switched off and the vessel was removed from the liquid helium dewar. By this time, all the H-atoms trapped in the graphite should have recombined to H<sub>2</sub> and desorbed from the graphite since, as found by Pirronello et al. (1999), hydrogen molecules desorb from the amorphous carbon within tens of seconds at 15-17 K. The ratio of the probabilities for H-atom recombination on a graphite surface vs that for H-atom reaction by quantum-mechanical tunneling with the graphite to yield CH<sub>4</sub> should be:

$$P_{recomb}/P_{react} = \pi a^2 \langle v \rangle s n_H / \nu_0 \exp[-(4\pi/h)(2m\Delta E)^{\frac{1}{2}} \Delta x]$$

where the recombination was calculated by Barlow and Silk (1976), after Hollenbach (1969) and Hollenbach and Salpeter (1970).  $a$  is the grain radius,  $\langle v \rangle$  is the mean thermal velocity of the gas-phase H-atoms,  $s$  is the H atom sticking probability ( $\sim 1$ ).  $n_H$  is the gas-phase H-atom density and  $m$  is its mass.  $\nu_0 = 10^{13} \text{ sec}^{-1}$  is the frequency of surface vibration of an adsorbed H-atom and  $\Delta E = 5500 \text{ cal mole}^{-1}$  is the activation energy of the reaction of an H-atom with graphite (Wood & Wise 1969). This yields at  $\sim 30 \text{ K}$   $P_{recomb}/P_{react} = 1.3 \times 10^{-10} n_H$ . Under our experimental conditions, a roughly estimated upper limit of  $n_H \gg 10^{12} \text{ cm}^{-3}$  near the graphite would result in an estimated  $P_{recomb}/P_{react} \gg 130$ , which would still allow a measurable rate of methane formation. With  $n_H = 10^3 \text{ cm}^{-3}$  in clouds,  $P_{recomb}/P_{react} \gg 1.3 \times 10^{-7}$ . *Namely, the major pathway will be hydrocarbon formation rather than recombination. This will be discussed later.*

### 3 Experiments with H, O and S-atoms at 78 K

A detailed description of the experiments is given in Bar-Nun (1975). Graphite powder 170-300 mesh, "specpure" from Johnson Matthey was used and the vessel was cooled by liquid nitrogen. H and O-atoms were produced by an RF discharge (Raytheon PGM-10) in H<sub>2</sub> and O<sub>2</sub> as described before. S-atoms were produced by a discharge in sulfur vapor from sublimation of sulfur powder ("sublimed" from Riedel-de Haen) at the end of the side arm, in the presence of 3 Torr of He. Some flow experiments were carried out with H and O-atoms, but will not be discussed here. The experimental results are shown in Table II.

**Table 2.** Product Distribution in the Various Experiments (static RF series)

Run	React. gas	P (Torr)	Temp (K)	Time (min)	Products- $\mu$ mole							
					CH <sub>4</sub>	C <sub>2</sub> H <sub>6</sub>	C <sub>3</sub> H <sub>8</sub>	C <sub>4</sub> H <sub>6</sub>	C <sub>4</sub> H <sub>10</sub>	CO	CO <sub>2</sub>	CS <sub>2</sub>
1	Ar	3	300	150	2.4-3	---	---	---	---	---	---	---
2	H <sub>2</sub>	3	78	60	6.8-1	2.0-2	<1.0-4	7.7-4	8.3-4	---	---	---
3	H <sub>2</sub>	30	78	60	2.1-3	2.3-4	---	---	---	---	---	---
4	H <sub>2</sub>	3	300	60	1.1-1	1.3-3	1.5-3	1.1-3	1.7-2	---	---	---
5	O <sub>2</sub>	3	78	180	---	---	---	---	---	4.5-1	3.7	---
6	S	3(He)	78	90	---	---	---	---	---	---	---	4.5

Again, the major hydrocarbon product is CH<sub>4</sub> with about a tenth of C<sub>2</sub>H<sub>6</sub> and some C<sub>3</sub>H<sub>8</sub> and C<sub>4</sub>H<sub>10</sub>. As discussed by Bar-Nun (1975), the C<sub>3</sub> and C<sub>4</sub> species are produced most likely in the gas phase at 78 K, while CH<sub>4</sub> and C<sub>2</sub>H<sub>6</sub> are produced on the graphite surface. Similarly, CO, CO<sub>2</sub> and CS<sub>2</sub> are produced on the graphite surface. N-atoms did not produce C<sub>2</sub>N<sub>2</sub>, which could have been expected by analogy to C<sub>2</sub>H<sub>6</sub>.

#### 4 Discussion

The major conclusion of these experimental studies is that in dense clouds where  $n_{\text{H}} = 10\text{--}1000 \text{ cm}^{-3}$ ,  $P_{\text{recomb}}/P_{\text{react}} = 1.3 \times 10^{-9}\text{--}1.3 \times 10^{-7}$  and the H-atoms will react preferably with bare graphite surfaces to produce mostly CH<sub>4</sub>, rather than recombine to form H<sub>2</sub>. The CH<sub>4</sub> and some C<sub>2</sub>H<sub>6</sub> would stay on T < 20 K surfaces and form a monolayer, on which further H-atom recombination to H<sub>2</sub> could proceed. Over time, UV photolysis and low energy cosmic rays could polymerize the hydrocarbons coating, leading to high molecular weight materials similar to Titan's Tholins (Bar-Nun et al. 1988), as well as eject some of the small molecules. In clouds at T > 78 K, CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, CO, CO<sub>2</sub> and, perhaps, CS<sub>2</sub> would desorb from the grain surface after their formation, leaving behind bare carbon surfaces. The Pirronello-Vidali group (1999) study of H-atom recombination on carbonaceous material is an important step in the right direction. I would like to encourage them to study as well the formation of CH<sub>4</sub> and other hydrocarbons under the same conditions.

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