THE FORMATION OF HYDROCARBONS AND IRON-HYDRIDES ON COLD INTERSTELLAR GRAINS-EXPERIMENTAL STUDIES

A. Bar-Nun[1], M. Litman[1], M. Pasternak[2] and M.L. Rappaport[2]
[1]Department of Geophysics and Planetary Sciences and
[2]Department of Physics and Astronomy,
Tel Aviv University, Tel Aviv, Israel

1. ABSTRACT

Cold hydrogen atoms at T $\geq$ 7K were shown experimentally to react with graphite grains at the same temperature to produce CH_4 and smaller amounts of C_2H_6, C_2H_4 and C_2H_2. At T < 20K the hydrocarbon mantle could polymerize to form carbonaceous substances, similar to those found in carbonaceous chondrites. Further encounters with H-atoms would result in their recombination on the hydrocarbon mantle around the grains. At higher grain temperatures, the hydrocarbons formed could be ejected into the gas phase.

Cold iron atoms at T < 5K were shown experimentally to react with molecular hydrogen in a T < 5K matrix. Mössbauer studies with ^{57}Fe demonstrated the formation of an Fe-H_2 bond. FeH_2 and FeH molecules could be formed on grains by encounters of iron atoms with either H-atoms or H_2 molecules.

2. INTRODUCTION

The recombination of H-atoms on grains to form H_2 molecules is by now well established. The two experimental studies which are reported here suggest that H-atoms and H_2 molecules could participate in additional reactions on grains' surfaces. The applications of these studies to the chemistry of interstellar clouds are discussed.

3. EXPERIMENTAL PROCEDURES AND RESULTS

3.1. The Hydrogen-graphite reaction

The experiments at 4.6 - 300K were performed in essentially the same way as those at 78 - 300K, which were reported earlier (Bar-Nun, 1975). The reaction vessel consisted of a quartz tubing 50 cm long and 2 cm I.D. with a side arm 10 cm long and 0.5 cm I.D. attached at the top.

B. H. Andrew (ed.), Interstellar Molecules, 367–371.

Several small pieces of pyrolytic graphite (General Electric) were placed at the bottom of the reaction vessel and outgassed at 1200K and 8×10^{-6} Torr for several hours. Hydrogen and helium (Matheson Research Grade) at pressures of 6 Torr each were introduced into the vessel, which was then lowered into a liquid helium dewar until the desired temperature was reached. A cavity of a 100W Kiva model MPG-4 microwave generator was then placed on the side arm and the discharge which generated the H-atoms was continued for 60 min. After the discharge was switched off the vessel was kept at the same low temperature for five more minutes and was then warmed up to room temperature before the products were analyzed by gas chromatography. The experimental results are shown in Table 1. The number of surface carbon atoms was determined by adsorption of argon at 77K and found to be $(1.0 \pm 0.5) \times 10^{17}$. Thus, the effective surface area of the graphite is six times larger than its geometric area. This study was described in detail by Bar-Nun et al (1979).

Table 1. Product Distribution in the Various Experiments

Run	Reactant			Temperature	Products, nmole			
	H_2	He	graphite	K	CH_4	C_2H_6	C_2H_4	C_2H_2
21	+			300	2.35	-	-	-
22	+	+		300	2.38	0.21	0.21	-
4 runs		+	+	300	0.44	-	-	-
35	+	+	+	300	10.37	-	-	-
46	+	+	+	77	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	-

3.2. The Iron-Hydrogen Reaction

A stream of molecular hydrogen or 10% hydrogen in argon and a stream of iron atoms from a crucible at ∿1000K were allowed to reach a cold substrate (1.5 or 4.2K), freeze there and react. The iron mixing ratio in the matrix was 2×10^{-3}. Mossbauer spectroscopy was used for analyzing the product while still at T < 5K. From the observed isomer shift ($\alpha = 0.42 \pm 0.03$ mm sec^{-1} with respect to metallic iron) and the isomer shift of FeF_2, it can be concluded that one of the iron's 4s electrons is transferred to the molecular orbitals of the hydrogen. A possible configuration of the molecule thus formed is $H_{Fe}H$. It is worth noting that all the iron atoms reacted with hydrogen and that at T > 5K

https://doi.org/10.1017/S0074180900072880 Published online by Cambridge University Press

the iron started to agglomerate into metallic grains because of the softening of the hydrogen matrix. This study was described in detail by Pasternak and Barrett (1978).

4. DISCUSSION

4.1. Hydrocarbon Formation

The results of the blank runs show that both the vessel and the graphite were free of organic contamination. The major product is methane but some ethane, ethylene and acetylene are also formed. At 4.6K practically all the hydrogen was adsorbed on the graphite and H-atoms were not available for the reaction. Yet, even at this temperature enough helium was left in the reaction vessel to cause thermalization of the H-atoms, which diffused along 50 cm from the side arm to the graphite.

In the context of reactions in cold interstellar clouds it is important to establish that the H-atom graphite reaction takes place at low temperature and not during the warming up to room temperature. H-atoms can be adsorbed on surface carbon atoms and possibly also between the carbon sheets in the graphite crystal which are separated by 3.4Å. The small surface area measured shows that Ar atoms cannot penetrate between the sheets and therefore, even if H-atoms do penetrate there, the products which are larger than Ar would not be able to diffuse out. Thus the observed reaction takes place at the surface. At 12K, 65 nmole of CH_4 were produced, consuming 1.6×10^{17} H-atoms, or on every surface carbon atom should be adsorbed an H-atom. For the reaction to take place during the warming up process, these atoms would have to remain adsorbed on the surface without recombining for at least 300 sec. Barlow and Silk (1976) estimated the time for an H-atom to hop from one site to the other by quantum-mechanical tunnelling as 10^{-5} sec. Even if the time is five orders of magnitude longer, which is very unlikely and would cause severe difficulties for H-atom recombination on grains in the clouds, the time for recombination would have been short in comparison with 300 sec. It can therefore be concluded that the hydrocarbon forming reaction indeed takes place at low temperature. From Barlow and Silk's (1976) probability for recombination and assuming quantum-mechanical tunnelling by hydrogen in the reaction with graphite, with an energy barrier of 0.23 ev (Wood and Wise, 1969) and a width of the barrier of $\sim$1Å, the ratio of probabilities of recombination vs reaction is $1.3 \times 10^{-10}\ n_H$, where n_H is the H-atom number density. Thus, even in cold interstellar clouds H-atoms would react with bare graphite grains rather than recombine on them.

4.2. Iron Hydrides formation

The major problem in this experiment is the high initial temperature of the iron atoms which are ejected from a crucible at $\sim$1000K.

https://doi.org/10.1017/S0074180900072880 Published online by Cambridge University Press

However, in the reaction in the matrix which consisted of 10% hydrogen in argon, the hot iron atoms had encountered several argon atoms before encountering a hydrogen molecule. During these encounters they were thermalized to the matrix temperature and, since all the iron atoms formed FeH molecules, it is apparent that the reaction takes place when all the reactants are at T < 5K. This could occur by quantum-mechanical tunnelling of the hydrogen molecules. The reaction $Fe+H_2 \rightarrow FeH + H$ is endothermic by $\sim$2.04 ev since the bond energy in H_2 is 4.47 ev and that of FeH according to Walker et al (1972), is 2.43 ev. Thus, FeH would not be formed from hydrogen molecules but could be formed by encounters of H-atoms and Fe-atoms on grains.

5. IMPLICATIONS FOR COLD INTERSTELLAR CLOUDS

In dense and cold clouds where $n_H \sim 10$ cm^{-3} all the H-atoms which remain on the bare graphite grains long enough would react with the surface carbon atoms to form methane and some other C_2 hydrocarbons. At T < 20K the hydrocarbons would be strongly bound to the grains (Watson and Salpeter, 1972) and form a monolayer around them. Further encounters with H-atoms would result in their recombination on the hydrocarbon monolayer. The hydrocarbon mantle could evolve chemically by irradiation with short uv and low energy cosmic rays (Watson and Salpeter, 1972) and could eventually polymerize. Such polymers are indicated by several IR emission bands in clouds (Knacke, 1977). Mantle formation could be inhibited by ejection of the hydrocarbons in very small grains or by photoejection or sputtering during cloud-cloud collisions, and in clouds with grain temperatures greater than 77K by thermal ejection (Bar-Nun, 1975).

Encounters of iron atoms with H-atoms on grains would result in the formation of FeH molecules, with absorption bands at 5900, 6400, 15600, 17100 and 33000 cm^{-1} (Walker et al, 1972). Similar hydrides of Cd, Mn, Co, Ni and Cu, all of which were formed experimentally (Walker et al, 1972), could be responsible in part for the depletion of these species as well as iron in the clouds. Encounters of Fe atoms with H_2 molecules on grains could result in the formation of FeH_2 species. The formation of these hydrides would not prevent metal grains formation, since their encounters with each other result in agglomeration, even at 5K, as demonstrated by the experiments.

REFERENCES

Barlow, M.J., and Silk, J.: 1976, Ap. J. 207, pp. 131.
Bar-Nun, A.: 1975, Ap. J. 197, pp. 341.
Bar-Nun, A., Litman, M., and Rappaport, M.L.: 1979. Submitted to Astron. & Astrophys.
Knacke, R.F.: 1977, Nature 269, pp. 132.
Pasternak, M., and Barrett, P.H.: 1978. Proceedings of "Workshop in Applications of Mössbauer Spectroscopy" Seeheim/Bergstrasse, W. Germany, April, 1978.

Walker, J.H., Walker, T.E.H., and Kelly, H.P.: 1972, J. Chem. Phys. 57, pp. 2094.
Watson, W.D., and Salpeter, E.E.: 1972, Ap. J. 174, pp. 321.
Wood, B.J., and Wise, H.: 1969, J. Chem. Phys. 73, pp. 1348.

DISCUSSION FOLLOWING BAR-NUN

Carruthers: The conclusion of your paper, then, is that H_2 cannot be formed by pure graphite grains, only coated graphite, or silicates, etc.? If correct, this conclusion may be of significance in the interpretation of the far-UV extinction curve. Perhaps hydrocarbon coating may be in part responsible for the steep rise below 1600 Å. In the directions showing both the steep rise and the 2200 Å "graphite" feature, such as ζ Oph, there is a great deal of H_2, but toward θ Ori, which has the 2200 Å bump but little far-UV rise, there is little or no H_2, although E(B-V) is the same.

Bar-Nun: Yes indeed, it seems that on bare graphite grains at low temperatures, H-atoms would react to form hydrocarbons rather than recombine to form H_2 molecules. I would like to suggest that, since at low temperatures a hydrocarbon mantle would form around the grains, H-atom recombination should be studied on frozen hydrocarbons rather than on bare graphite.