

MOLECULE FORMATION ON GRAIN SURFACES*

E. E. SALPETER

Cornell University, Ithaca, N.Y., U.S.A.

I will discuss the formation of molecules AB from two atoms or radicals A and B only for cases where the reaction $A + B \rightarrow AB$ is exothermic. The efficiency of this reaction on the surface of an interstellar dust grain is the product of two factors: (i) the 'sticking coefficient' or probability that the first radical hitting the grain surface from the interstellar gas becomes thermalized and sticks to an adsorption site; (ii) the recombination efficiency or probability that the first adsorbed radical will remain adsorbed, rather than evaporating, during the time required for the second radical to hit the grain, be adsorbed and find its partner.

I will consider only grains inside interstellar H I clouds which are at least 'medium-dark', densities of $\gtrsim 50$ H-atoms cm^{-3} and an extinction optical depth in the visible of $\tau_v \gtrsim 0.5$, say. Clouds of such modest extinction are in fact quite common and one can estimate [1] that about one quarter of all the interstellar gas resides in such clouds. Such clouds are not essential for forming the molecules but, as we have heard earlier in this discussion, are needed to shield the molecules from photo-disintegrating starlight. However, dark clouds are also beneficial to formation in keeping the gas temperature low ($\lesssim 100\text{K}$) which keeps the sticking coefficient [2] high ($\approx \frac{1}{2}$).

TABLE I

(Assuming 300 H/cc) one H-atom:

Hits another H-atom	≈ 10 yr
Hits a dust grain	$\approx 10^6$ yr
Processed through a star	few $\times 10^9$ yr
Enters H II region with Lyman-continuum	$\approx 10^8$ yr
(H_2 photodissociated)	≈ 100 yr

Before discussing the recombination efficiency, Table I compares the potential of formation on grain surfaces with two 'rival' formation modes for molecules: a gas atom hits a (hydrogen) atom about 10^5 times more often than it hits a dust-grain. Thus, if a radiative two-body recombination has a cross-section more than 10^{-5} times the gas-kinetic cross-section, recombination in the gas-phase will dominate for this particular molecule. On the other hand, during the lifetime of the Galaxy, a gas atom hits a dust-grain about 10^3 times more often than it is processed through a star. Thus, if a particular molecule can be formed (without being destroyed immediately) on grain surfaces in moderate clouds with an efficiency of more than 10^{-3} , then such

* Supported in part by the U.S. National Science Foundation.

clouds will produce more molecules than could be produced in (a) extremely dense globules which are about to become a star or (b) surfaces of stars and ejected by stellar winds.

Now for the recombination efficiency: an atom or radical adsorbed to a grain surface with grain temperature T_{gr} , experiences a lattice vibration about every 10^{-12} sec, but has to wait about 30 sec till another (hydrogen) atom hits the surface with which it can combine. An adsorbed atom, with average adsorption binding energy D , must survive about e^{30} lattice vibrations without evaporating to give good recombination efficiency. Recombination will then be highly efficient if the Boltzmann factor $\exp(D/kT_{gr})$, by which evaporation per lattice vibration is inhibited, is even larger – i.e. if $D/kT_{gr} \gg 30$. Some time ago R. Gould and his collaborators [3] considered that this inequality held, but during an interim period a few years ago some pessimism developed because estimates for the adsorption binding energy D , at least for atomic hydrogen, were rather low [4] and rather high values for the grain temperature were fashionable then. By now, however, complete optimism has returned (at least to my mind) that recombination is almost 100% efficient, at least for the formation of H_2 -molecules from H-atoms. First of all, estimates for grain temperatures in clouds are now lower ($T_{gr} \lesssim 25$ K) because more realistic grains with some impurities in them radiate more efficiently in the infrared and also because grains in a cloud are partially shielded from starlight heating (see, for instance, [5]). Secondly, there must be at least some surface sites on realistic grains where the binding energy for a hydrogen atom (or other radical) is appreciably greater than the $\approx k \times 400$ K estimated for pure Van der Waal physical adsorption. Even on pure graphite grains some full chemical valence bonds [6] are possible, but I feel that there must be plenty of surface defects (e.g. results from cosmic ray bombardment) which must present considerably more binding to an atom or radical than pure Van der Waal forces – a kind of ‘partial valence bond’. Hollenbach [2] has shown that even a few sites of such enhanced binding are sufficient to give excellent recombination efficiency.

My complete optimism about the efficiency for $H + H \rightarrow H_2$ has to be qualified for the formation of other molecules for a reason which may sound paradoxical, namely the possibility that binding energies may be too high. Atomic hydrogen on metal surfaces experiences chemisorption binding energies of order ≈ 1 eV $\approx k \times 10^4$ K. Interstellar dust-grains are more inert than metals and binding energies will be less, but they might not be much less for atoms and radicals. For $H + H \rightarrow H_2$ this possibility can only help not hinder – H is the most common gas atom hitting a dust grain, sooner or later another H-atom will stick near it, H_2 -formation is still exo-energetic, and H_2 , being a saturated structure, does not have a large adsorption energy and the molecule can eventually evaporate. For other molecules, however, there are various uncertainties.

Diatomic hydrogen compounds CH, NH, OH, etc. can certainly form on grain surfaces from their constituent atoms in analogy with formation of H_2 . However, these radicals are themselves unsaturated structures and may (or may not) have large adsorption binding energies. If so, they will remain on the grain until they react with

further H-atoms and finally evaporate as saturated structures, CH_4 , NH_3 , H_2O , etc. In these cases, then, some hydrogen compounds will certainly form with good efficiency and the only uncertainty is which one. Incidentally, if the cloud is shielded enough for a radical like OH not to photo-dissociate in the gas-phase, reactions like $\text{OH} + \text{H} \rightarrow \text{H}_2\text{O}$ will also proceed efficiently on the grain-surfaces. Similarly, if CO is present in the gas, for instance, it should be easy to form H_2CO on the surface (this is true whether the hydrogen in the gas-phase is mainly in atomic or molecular form).

The situation is more uncertain for the formation of a molecule out of two radicals, each of which contains an atom of carbon or heavier, e.g. $\text{C} + \text{O} \rightarrow \text{CO}$. These radicals will have a surface binding energy comparable to that for a hydrogen atom. If these binding energies are an appreciable fraction of an eV, thermal diffusion on the cold surface is negligibly slow and quantum mechanical (barrier penetration) mobility is very much slower for the radicals than for H, because of their greater mass. It might then happen that each radical remains stuck on its own surface site, whereas H-atoms arriving later can still wander around the surface and find the radicals. If that is the case, then, C and O atoms hitting the surface would never form CO but only CH_4 and H_2O . To settle these uncertainties, better estimates for chemisorption binding energies will be required.

References

- [1] Hollenbach, D., Werner, M., and Salpeter, E.: 1971, *Astrophys. J.* **163**, 165.
- [2] Hollenbach, D. and Salpeter, E. E.: 1970, *J. Chem. Phys.* **53**, 79; 1971, *Astrophys. J.* **163**, 155.
- [3] Gould, R. and Salpeter, E.: 1963, *Astrophys. J.* **138**, 393; Gould, R., Gold, T., and Salpeter, E.: 1963, *Astrophys. J.* **138**, 408.
- [4] Knaap, H., v.d. Meydenberg, C., Beenakker, J., and Van de Hulst, H.: 1966, *Bull. Astron. Inst. Neth.* **18**, 256.
- [5] Werner, M. W. and Salpeter, E. E.: 1969, *Monthly Notices Roy. Astron. Soc.* **145**, 249.
- [6] Stecher, T. P. and Williams, D. A.: 1966, *Astrophys. J.* **146**, 88.