PHOTOCHEMISTRY OF ATOMS AND MOLECULES IN THE ADSORBED STATE

H. D. BREUER and H. MOESTA
Institut für Physikalische Chemie der Universität Bonn, Bonn, D.B.R.

Assuming interstellar dust particles being composed at least partly of materials with catalytic activity or of refractory metals and being exposed to the radiation field of the Sun or other stars they can favour the formation of molecules as combinations of the most abundant gases H, C, N and O mainly for three reasons:

(1) By the adsorption at the surface of dust particles the collision probability for two or more atoms is greatly enhanced with respect to the gas phase.

(2) Because of the adsorption bond the excitation and dissociation energies are shifted to lower values.

(3) For highly exothermic reactions dust particles can absorb the excess energy and thus lead to the formation of molecules which in the gas phase can be formed only by three body collisions.

To emphasize the effect of energy shifting on photochemical processes Figure 1 shows, for example, the solar spectrum between 1000 Å and 2600 Å. The intensity is plotted in a logarithmic scale. Reasonable intensities are emitted only above 2000 Å. Even Ly-α at 1216 Å is only about 1% of the 2500 Å radiation. By the bathochromic effect of the adsorption the energy levels of the atoms and molecules which usually are in the vacuum UV region are shifted to a part of the spectrum where sufficient intensity is available.

Measuring the wavelength dependence of photo-reactions for some gases adsorbed on different metal surfaces we found reactions in wavelength regions where these gases are transparent in the gas phase*. Identification of the photo-products was done by a very sensitive mass spectrometer. Figure 2 shows the mass spectrum for CO adsorbed on tungsten and irradiated by a Hg-resonance lamp ($\lambda = 2537$ Å). The molecule is excited by the radiation and forms an unstable intermediate. Dissociation leads to highly reactive carbon and oxygen atoms at the surface. These atoms can react with undissociated molecules or already formed radicals to the observed products according to the following scheme:

$$\begin{aligned} CO + h\nu &\rightarrow CO^* \\ CO^* &\rightarrow C + O \\ CO + C &\rightarrow C_2O \end{aligned}$$

* For experimental details see:
H. Moesta and H. D. Breuer: *Naturwissenschaften* **55** (1968) 650; H. Moesta and N. Trappen: *Naturwissenschaften* **57** (1970) 38; H. D. Breuer, H. Moesta, and N. Trappen: *Chemiker-Z.* **94** (1970) 129; H. Moesta and H. D. Breuer: *Surface Science* **17** (1969) 439; and H. Moesta, H. D. Breuer, and N. Trappen: *Ber. Bunsengesellschaft physikal. Chemie* **73**, (1969) 879.

De Jager (ed.), Highlights of Astronomy, 432–437.

$$CO+O \rightarrow CO_2$$
$$C_2O+O \rightarrow C_2O_2$$
$$C_2O+CO \rightarrow C_3O_2.$$

A co-adsorption of CO and CH_4 results in a much more complex mass spectrum. Because of the dissociative adsorption of methane both atomic hydrogen and hydrocarbon radicals are available for the photo-reaction. Figure 3 shows the whole spectrum up to mass number 72. An analysis of the spectrum shows fragmentation peaks typical for aldehydes. To ensure this reaction mechanism we performed the experiments under the same conditions with CD_4 instead of CH_4. Figure 4 shows for comparison a part of the W–CO+CH_4 spectrum and in the lower section the spectrum for W–CO+CD_4. In the upper part H_2CO occurs at mass number 30 and HCO as a fragmentation product in the ion source at mass number 29. With deuteromethane D_2CO occurs at mass number 32 and consequently DCO at mass number 30. The peaks at $m/e=31$ and $m/e=29$ result from the hydrogen content in the CD_4. These experiments show the formation of formaldehyde at a surface irradiated by 2537 Å. Higher aldehydes which may be formed as well cannot be detected for experimental

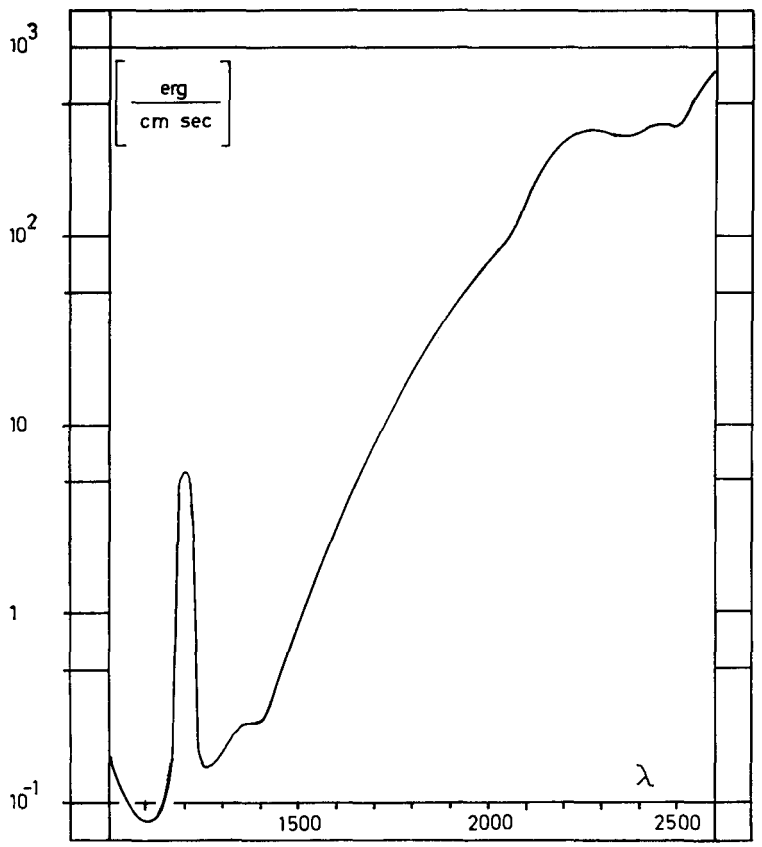

Fig. 1.

https://doi.org/10.1017/S153929960000040X Published online by Cambridge University Press

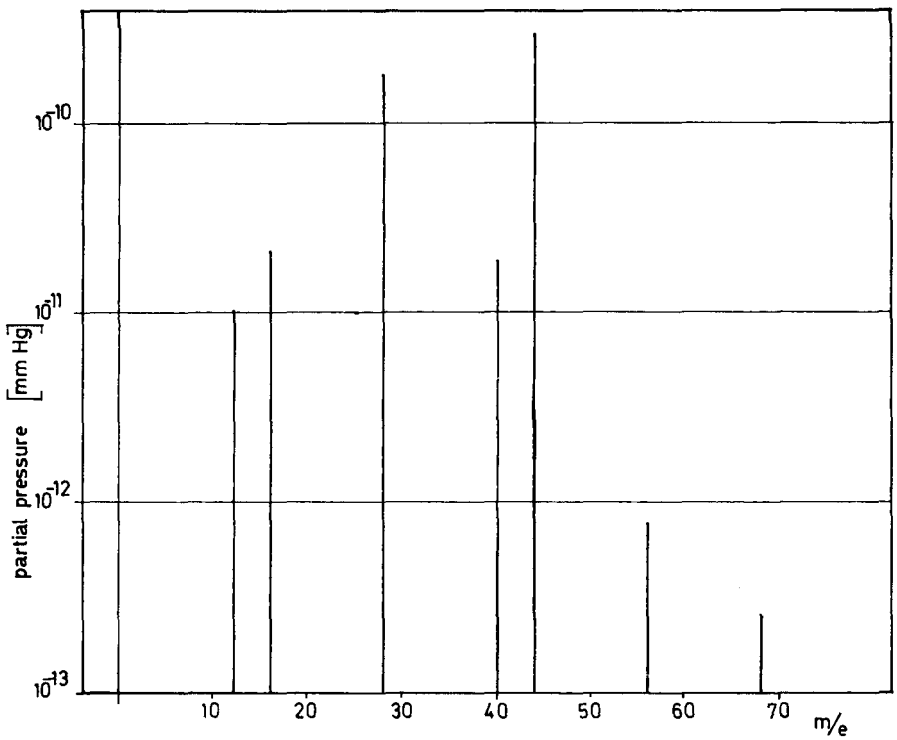

Fig. 2.

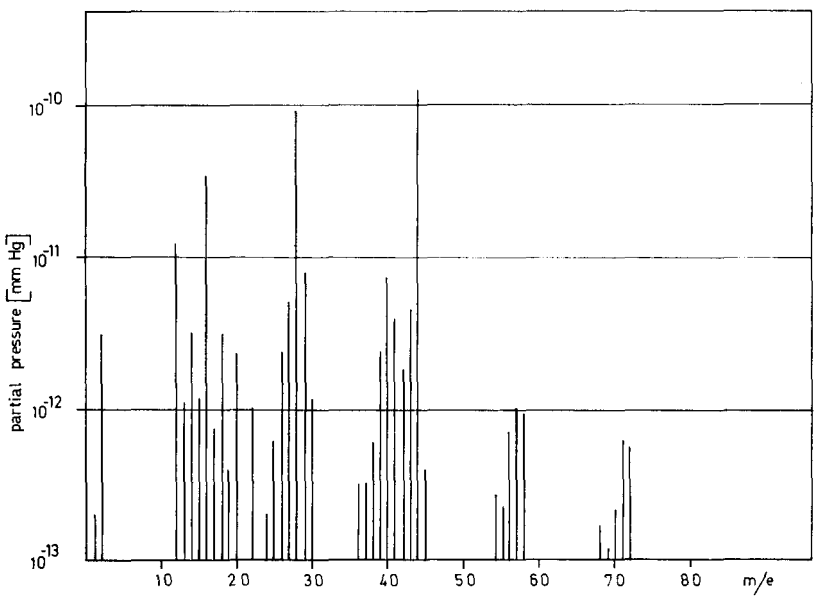

Fig. 3.

https://doi.org/10.1017/S153929960000040X Published online by Cambridge University Press

reasons. Irradiation of co-adsorbed CO, H_2 and N_2 on tungsten leads to the following products:

$m/e = 25$ C_2H
26 CN
27 HCN
29 N_2H
30 NO; N_2H_2
38 C_2N
39 C_2HN
40 C_2H_2N
41 CH_3CN
44 N_2O
46 NO_2.

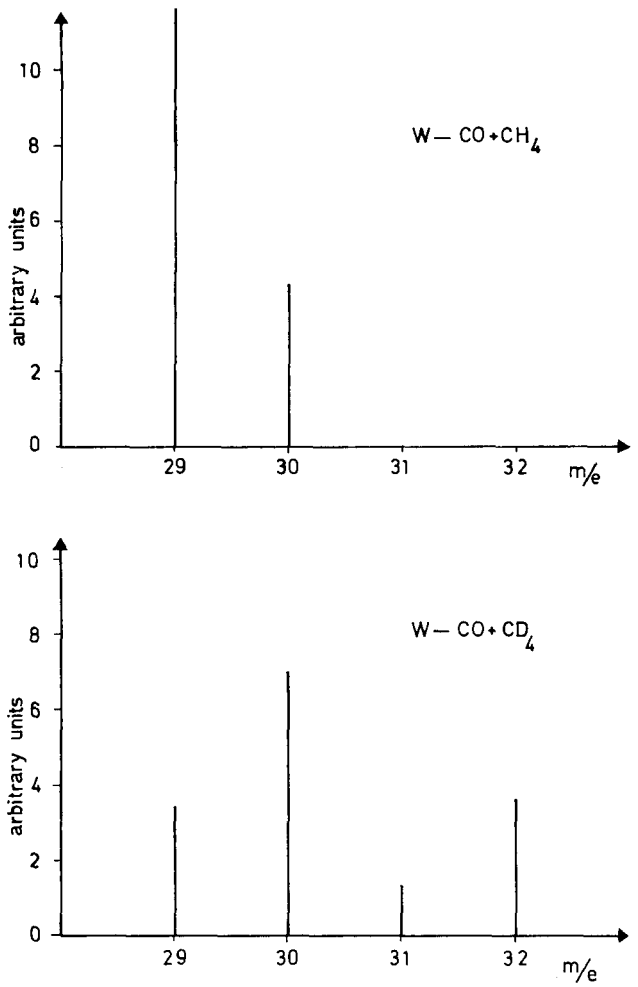

Fig. 4.

https://doi.org/10.1017/S153929960000040X Published online by Cambridge University Press

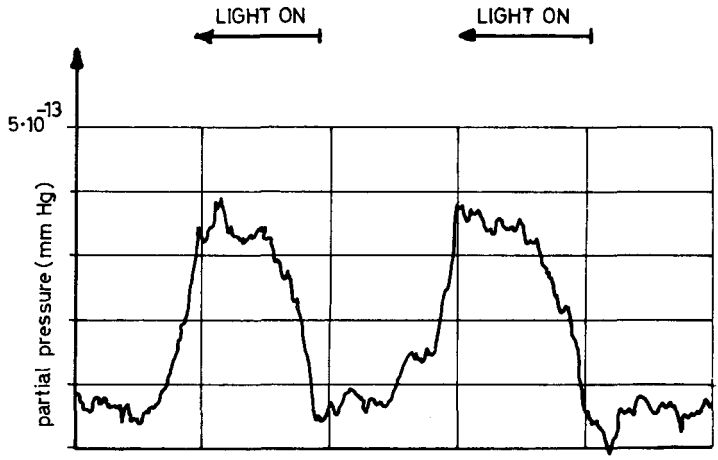

Fig. 5.

An analysis of this spectrum shows that beside the molecules NO, N_2O and NO_2 we find fragmentation peaks of acetonitrile (CH_3CN). The intensities of the CN and HCN peaks however are by far too high as to originate in the fragmentation of CH_3CN. So these molecules must be formed in the photo-reaction at the surface. Ammonia which is formed as well at the surface is insensitive to the 2537 Å radiation. Searching for cyanoacetylene (C_3HN) which recently was detected in interstellar space by its microwave spectrum (B. E. Turner, 1970) we found a photo-product at mass number 51. Figure 5 shows the increase and decrease of this species synchronous with the irradiation. The production rate is about 20 times lower than the rate for CN and HCN formation. However we have not yet made any experiments to ensure the identification.

Our choice of metals as adsorbing surfaces may not be representative for the composition of interstellar dust particles, but our experiments show that in an adsorbed layer, molecules can be formed at very much lower radiation energies than in the gas phase.

This work was sponsored by the Deutsche Forschungsgemeinschaft, which gratefully is acknowledged.

DISCUSSION

Solomon: If such molecules are formed by ultraviolet light, why are they formed exclusively in dense dust clouds where the ultraviolet flux is low?

Sagan: Let me attempt to answer. In experiments reported in *Science* last April we passed a single temperature pulse through a mixture of CH_4, NH_3, H_2O and so on in a shock tube. The physics is a quenched thermodynamic equilibrium with radicals recombining cold because of the short dwell times in the shock. We produced amino acids in extraordinarily high yields – more than one third of the ammonia was converted into amino acids in a single shock; and the intermediaries very likely included nitriles and aldehydes. Shocks are expected in dense interstellar clouds. Because of the high efficiency of shock synthesis, I would suggest that they make a significant contribution to interstellar organic chemistry.

Solomon: If it's so easy, why did the origin of life take so long?

Sagan: There's a long way between formaldehyde and, say, you!

Very similar results have been obtained in gas phase reactions in laboratory glassware in work devoted to problems of the origin of life or of the composition of planetary atmospheres. For example, ten years ago we reported work – in which we sparked with a corona discharge a mixture of CH_4, NH_3, and H_2O in an excess of H_2. The molecules produced in highest yield were HCN, CH_3CN, HCHO, CH_3CHO, C_2H_2, C_2H_4, and C_2H_6 – a list of small organics which might be of use to workers in the interstellar microwave line identification problem. In addition such experiments produce a great many more complex molecules, including amino and hydroxy acids, sugars, purines and pyrimidines, porphyrins and higher hydrocarbons, including polycyclic aromatics. The structure and absorption properties of polycyclic aromatic hydrocarbons, incidentally, are quite close to those of graphite, a widely advertized candidate constituent for the interstellar grains. It is also quite remarkable that many of these molecules are produced under a wide range of temperatures, pressures, initial mixing ratios, and energy sources.