

ZEOLITE AS CATALYSTS FOR THE SYNTHESIS OF AMINO ACIDS AND PURINES

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Abstract—This paper attempts to show that the catalytic properties of zeolitic material may play a role in the synthesis of simple biological molecules from gases commonly found in extraterrestrial atmospheres. Linde *X* and *Y* molecular sieves cation-exchanged by Ca^{2+} and Fe^{3+} have been heated in the presence of carbon monoxide and ammonia. Amino-acids and u.v. absorbing substances identified by paper chromatography have been extracted from the solid. HCN, the basic molecule involved in the synthesis of those substances has been detected in the gas phase. It is proposed, on the basis of i.r. results, that the amino-acids are hydrolysis products of an undefined polymer.

INTRODUCTION

AMONG extraterrestrial molecules that could have been the raw materials for the evolution into simple biologically significant molecules, NH_3 , CO, H_2 , H_2O , CH_4 and CO_2 are the most abundant (Fox *et al.*, 1970). Sulphur and phosphorus are common in magnetic crusts. In the later stage of the condensation process of planetary components, organic compounds would have been synthesized by thermal reactions in highly reducing media, the reactions being catalyzed eventually by silicate surfaces and/or activated by radioactive radiations confined to the crust of the earth. Volcanic activity on the primitive earth was likely to be much greater than that of today. A common mineral of volcanic ashes is the so-called allophane (Fieldes and Schofield, 1960), which is essentially a poorly organized silico-alumina, quite similar to those used as cracking catalysts. Zeolitic types of materials can also be found in volcanic glasses (Hay, 1966). Although the catalytic properties of these crust minerals are quite familiar to those working in the field of heterogeneous catalysis, these investigators have never been interested in chemical processes involving the simple molecules that have been found in the interstellar space or in the atmosphere of extraterrestrial bodies.

Neglecting even the catalytic aspect, one of the advantages of considering these processes as occurring inside an adsorbed phase is to avoid criticisms towards experiments carried out in the laboratory. For instance the use of an homogeneous liquid, or gaseous phase at much higher pressures or concentrations in reactants than those which

might have prevailed in the primitive atmosphere (see, for instance, the controversy between Hulett, Wolman *et al.* and Fox *et al.* (1971). High energy radiation used by several authors would have had a destructive action on the primitive biological molecules (Fox, 1971). The adsorption properties of zeolites are so powerful that, at liquid air temperature, a 10^{-4} atm pressure of CH_4 suffices to fill up the zeolitic cavities with physically adsorbed molecules. Molecules with dipolar moments such as H_2O , NH_3 , CO and HCN are still more strongly adsorbed, even at higher temperature.

This paper attempts to describe preliminary results of some experiments in which the catalytic activity of molecular sieves (Linde *X* and *Y*), cation exchanged by Ca^{2+} and Fe^{3+} , was investigated with respect to a mixture of $\text{CO} + \text{NH}_3$ at 300°C . In this preliminary work neither the kinetics of the reaction nor the quantitative yields have been studied, the emphasis has been on the nature of the reaction products obtained under various conditions.

PROCEDURES

Catalysts and reagents

The Na-*X* and Na-*Y* Linde sieves were cation exchanged by Ca^{2+} or by Fe^{3+} by four treatments at room temperature with the corresponding N chloride solutions. The salt excess in the pores was removed by washing the solid with distilled water until disappearance of the chloride anion. The zeolitic structure of the Ca-sieve was stable at the temperature used in the experiments. A few experiments were done on a Fe-*X*-sieve. Saturation with Fe^{3+} resulted in a partial breakdown of the zeolitic structure, whereas the Ca-sieve was found unaffected by this treatment.

The Na-*X* only was first treated for 24 hr in a 10% H_2O_2 solution at 75°C in order to remove most

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of the organic impurities adsorbed from the atmosphere.

CO and NH₃ of chemical purity, were dried but not further purified. In a few cases, the gases were passed through a preactivated zeolite bed in order to remove possible contaminants. It must be emphasized that in all cases small amounts of water were present in the reacting system.

Apparatus

The main characteristics of the instrument, shown in Fig. 1, are; (1) the generalized use of greaseless stopcocks (Viton membrane) in order to prevent the adsorption and the further reaction of vacuum grease vapor on the catalyst (the vacuum line being protected by two cold traps); (2) an all-glass electromagnetic circulation pump (1); (3) a thin bed reaction cell (2), surrounded by an electric furnace; (4) a sampling device consisting of a trap (4), where the condensable reaction products could be collected and isolated.

The ground seals of (2) and (4) are greaseless and made from teflon-viton "O" rings. The gases are stored in flasks (5). The pressure change during the reaction is followed on M_1 whilst the partial pressures of the reagents before introduction are read by monometer M_2 . A Töpler pump (3) is used for introducing the gases.

The saturated and washed catalyst was oven-dried at 110°C, introduced into the reactor (2) and outgassed at 330°C under 10^{-5} torr.

One experiment was performed on an auto-coherent Ca-Y film placed in an i.r. cell, connected

to the main circuit in the place of trap (4), Fig. 1. The cell could be heated and evacuated in such a way that the reaction could take place in the same conditions in both the reactor 2 (Fig. 1), and in the cell.

ANALYTICAL PROCEDURES

HCN was isolated in trap 4 (see Fig. 1) which could be connected to a system similar to that used by Gettler and Goldbaum (1947) for traces determinations. The development of the coloration characteristic to Prussian blue indicated the presence of hydrogen cyanide. Amino-acids were analyzed by the classical paper chromatography technique.

The zeolite was first outgassed to remove the excess of gas mixture. The solid was then extracted three times with 3 ml of a 10^{-2} N HCl solution. The liquid was centrifuged and freeze dried. The solid residue was passed on a 5" Dowex 50 column and the amino-acids were then eluated with 1.5 M NH₄OH. Excess ammonia was removed and the solution was lyophilized.

The solid was dissolved in 1-2 ml of a (1-1) methanol-water mixture. The solution, centrifuged if necessary, was then analyzed by paper chromatography using a butanol-acetic acid-water mixture (30, 7.5 and 12.5 volumes respectively). For the two dimensional separation, phenol was taken as second solvent.

The crystallinity of the zeolite was checked with a Philips X-ray diffractometer using Ni-filtered, CuK_α radiation ($\lambda = 1.5418 \text{ \AA}$) and a Geiger

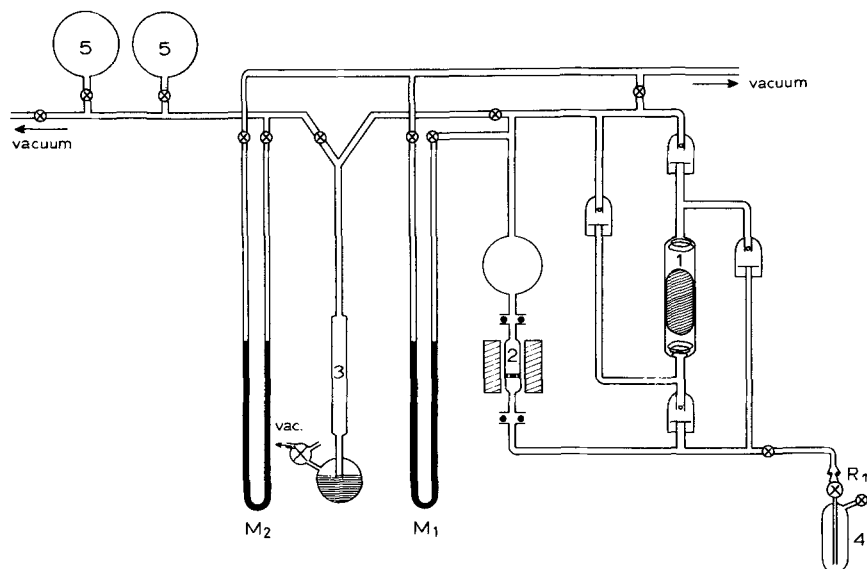


Fig. 1. Equipment used in this work. For description, see text.

detector. The tube was operated at 40 kV and 20 milliamp. The goniometer scanning was 1° 2θ/min.

The i.r. spectrograph (Beckman IR 12) was scanned at 0.5 μ/min. The gain was between 6 and 8% and the slit was 3 times the standard slit.

EXPERIMENTAL RESULTS

The conditions of temperature and pressure of some significant experiments performed on the X and Y zeolites are given in Table 1. Except for run 5, the zeolite (0.5 g) was pretreated under vacuum at 325°C during 20 hr.

The Ca-sieves did not undergo any significant structural change in those experiments, whereas the structure of Fe-X was appreciably damaged.

As it is shown in Table 1, CO + NH₃ react to give HCN, on both Ca and Fe sieves. The yield of gaseous HCN, roughly estimated from the intensity of the blue coloration, was in the range 10⁻³ to 10⁻⁶ mole.

In all the experiments carried out, amino-acids and u.v. absorbing products were always detected.

Some experiments were duplicated and the results were found to be satisfactory both in gas consumption and in the reaction products. Only when P_{CO}/P_{NH₃} was below 0.5 HCN could not be detected in the condensed phase.

Figures 2 (row II) and 3 show typical one-dimension chromatograms obtained from the extracts of the solids corresponding to experiments using Fe-X and Ca-Y sieves respectively. The corresponding R_f values are summarized in Table 2, together with the compounds to which they are attributed.

From this table, it can be seen that if amino-acids and u.v. absorbing substances are detected whatever the ionic form of the zeolite, a closer examination reveals differences in the nature and the number of those substances. Only three amino-

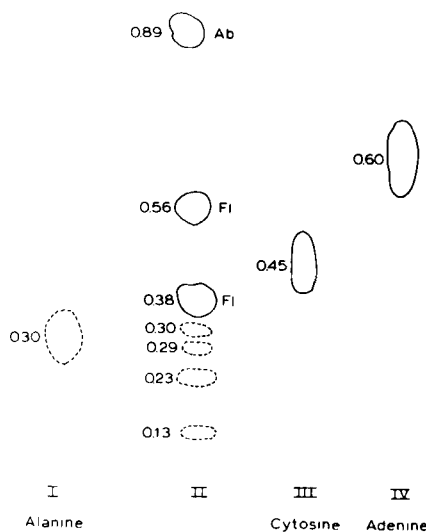


Fig. 2. One-dimension paper chromatogram of amino-acids and u.v. absorbing and fluorescent substances condensed on a Fe-X sieve (experiment 6) I, III and IV: reference alanine, cytosine and adenine respectively; II extract from Fe-X (exp. 6) Ab: u.v. absorbant; FI: u.v. fluorescent.

acids are commonly produced on both zeolites: glycine and/or aspartic acid, threonine and alanine. Among the u.v. absorbing substances, only one or two with R_fs of 0.38 and 0.65 (0.89) can possibly be common to the Ca- and Fe-sieves.

It is very interesting to point out the possible presence of phenylalanine. The reason why this amino-acid is detected only in two runs is not yet understood. The main difference in the experimental procedure lies in the time of the reaction. The P_{CO}/P_{NH₃} ratio does not seem to be involved,

Table 1. Experimental conditions and reaction products

Run	P _{in.} (torr)	P _{fin.} (torr)	P _{CO} /P _{NH₃} in	Temp. (°C)	Time (days)	HCN	Amino-acids	U. V. abs. subst.
Ca-X VII	376.0	279.2	0.7	250	2	not determ.	+	+
II	333.0	284.3	1.0	325	2	not determ.	+	+
IV	344.0	not det.	1.4	325	1	+	+	+
III	370.0	351.7	1.2	325	5	not determ.	+	+
Ca-Y 4I	178.7	142.7	0.5	325	5	-	+	+
7	258.4	209.4	1.0	250	6	+	+	+
5*	248.1	not det.	1.0	325	8	+	+	+
3II	172.1	167.0	2.0	325	5	+	+	-
Fe-X 6	358.4	209.4	1.0	325	4	traces	+	+
8	290.6	238.0	1.0	325	4	-	+	+

*Not pretreated.

Table 2. R_f values of amino-acids and puric bases and their attributions

R_f values	Compounds to which R_f values are attributed	Fe-X (see II Fig. 2)		Ca-Y (see Fig. 3)		
		3 II	4 I	4 II	5	7
0.11	Histidine	-	-	-	-	-
0.13	Lysine	+	-	-	-	-
0.15	Arginine	-	-	-	-	-
0.22	Serine	-	+	+	+	+
0.23	Aspartic acid and/or Glycine	+	+	+	+	+
0.26 (0.29)	Threonine	+	+	+	+	+
0.30	Alanine	+	+	+	+	+
0.35*	not identified	+	+	+	+	+
0.38*						
0.40*	not identified	-	+	+	+	+
0.45}	Cytosine	-	+	+	+	+
0.47}						
0.48†	not identified	-	-	+	-	+
0.56*	not identified	+	-	-	-	-
0.60	Phenylalanine and/or leucines	-	-	-	+	+
0.65†}	Adenine	+	+	+	+	+
0.89†}						

*U.V. fluorescent; †U.V. absorbant.

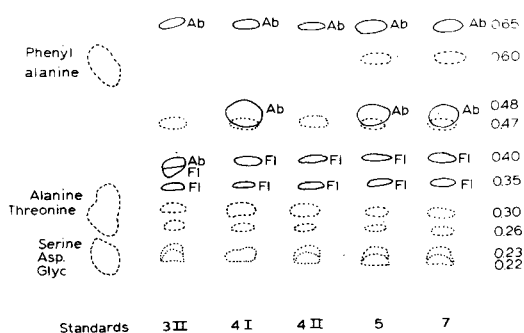


Fig. 3. One-dimension paper chromatogram showing the different amino-acids and u.v. absorbing and fluorescent substances extracted from a Ca-Y sieve. 3II, 4I, 4II, 5 and 7 refer to the experiments, Table 1. Ab: u.v. absorbing; Fl: u.v. fluorescent.

since on Ca-X, this amino-acid has not been detected.

As indicated in Table 2, the different u.v. absorbing substances have not yet been identified. Since HCN has been detected, they can be accounted for most probably by the presence of different polymeric forms of HCN, all of them being u.v. visible substances.

Two dimensional paper chromatograms obtained from the experiment 6_{II} performed on Fe-X, in the same conditions as in 6_I (Table 1) are shown in

Fig. 4. Only the weight of the catalyst was two times greater.

The spots on the right side of Fig. 4 indicate the position of the u.v. absorbing substances after the butanol-acetic acid-water separation. Their traces were lost after the second direction migration (phenol-ammonia).

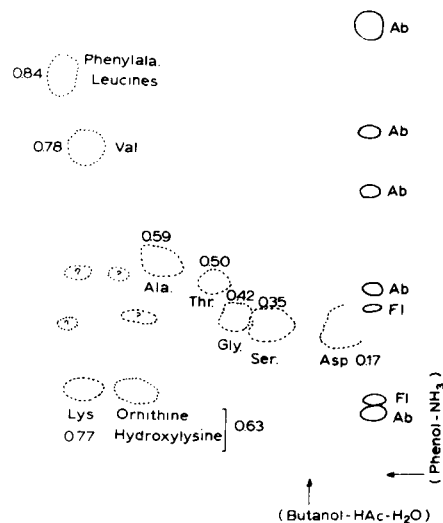


Fig. 4. Two-dimensions paper chromatogram showing the amino-acids and puric bases after reaction 6_{II} on Fe-X sieve.

The chromatogram reveals the presence of at least 9 amino-acids and possibly 13, and of 7 u.v. absorbing substances. Valine and phenylalanine (or leucines) were absent on the chromatogram shown in Fig. 2.

I.R. results

Experiment 5 (Table 1) was carried out under the same conditions on a bulk zeolite sample and on an autocohesive film in an i.r. cell which was connected in the place of cell 4 in Fig. 1. The cell was heated at the same temperature as the bulk zeolite. The i.r. spectra are shown in Fig. 5.

The vibrations at 2100 and 2000 cm^{-1} in spectrum B (the latter appearing at 1975 cm^{-1} in A) disappear after outgassing at 200°C. They are attributed to adsorbed CO and HCN, both species absorbing in this frequency range, though generally at slightly higher values (Kozirovski and Folman, 1966; Angell and Schaffer, 1966).

The most striking changes occur in the region between 1800 and 1350 cm^{-1} .

The broad bands at 1650 and 1470 cm^{-1} respectively after heating at 100°C become separated. After further heating, the first band develops and splits into several well defined bands whereas the second band becomes somewhat narrower and increases in relative intensity. A band at 1735 cm^{-1} , observed throughout all the spectra, is not affected

by the heat treatment. The vibration at 1690 cm^{-1} seems to be already present in A, and its intensity increases together with the removal of the broad band near 1640 cm^{-1} . This latter band becomes narrower in D and splits into two others at 1658 and 1625 cm^{-1} . The 1575 and 1350 cm^{-1} vibrations appear together after the film has been heated under vacuum at 200°C for 10 hr.

The first impression given by Fig. 5 is that of an undefined complex assemblage which, by some sort of rearrangement, develops into simpler molecular species.

The assignment of the different absorption bands is difficult because different functional groups absorb in this region. Indeed we are dealing with complex molecules differing in size and nature. According to the chromatographic results two classes at least are known, namely amino-acids (including possible small-size peptides) and puric substances.

For those two classes, whatever the actual molecular species, common functional groups absorb at roughly the same frequencies.

The 1735 cm^{-1} vibration can be assigned most probably to un-ionized COOH groups.

The 1690 cm^{-1} vibration can be accounted for by either C=O stretching (Bellamy, 1958) and/or by the N-CO amide I band and/or by a C=N stretch in imines or in unsaturated nitrogen compounds. Fripiat *et al.* (1966) have observed this band at 1676 cm^{-1} in adsorbed glycylglycine. The bands at 1658 cm^{-1} and at 1625 cm^{-1} could be assigned to the COO⁻ asymmetric stretching and to asymmetric NH₃⁺ deformations respectively.

CON-NH combination band, again according to Fripiat *et al.* (1966), could account for the absorption at 1575 cm^{-1} , whereas the 1350 cm^{-1} could be due as well to NH₂ scissoring as to $\delta(\text{CH}_3)$ or $\delta(\text{NH}_3^+)$. The 1500–1400 cm^{-1} range contains several unresolved bands. In this region a COO⁻ symmetric stretching (1410–1430 cm^{-1}) as well as the NH₃⁺ (near 1460 cm^{-1}), CH₂ (near 1430–1440 cm^{-1}), CH₃ (asym. and sym. 1485–1460 cm^{-1}) deformations may contribute to the broad observed band.

Hayatsu *et al.* (1968) obtained from a CO-H₂-NH₃ 1:2:0.4 gas mixture reacted at 600°C on an iron meteorite a non-volatile extract in which they identified urea, biuret, melamine, ammeline and adenine. The i.r. spectra showed vibrations at 1780, 1695, 1600, 1570, 1340 cm^{-1} and other at shorter wavelengths. They did not give an interpretation of their spectra.

DISCUSSION

The reaction of CO and NH₃ on Ca- and Fe-molecular sieves has led to the condensation on the

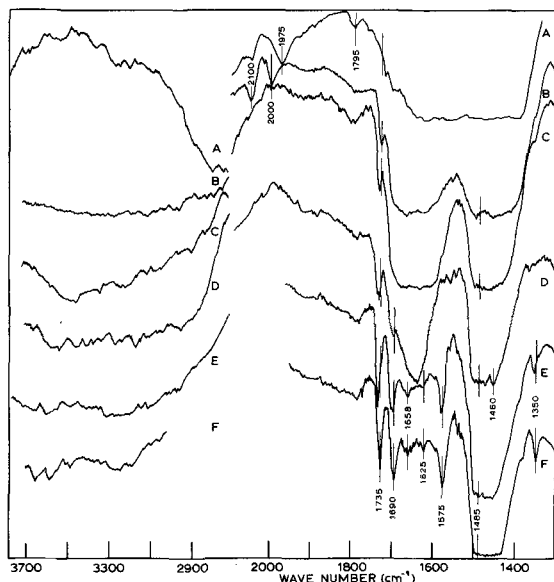


Fig. 5. I.R. spectra recorded for a coherent film of Ca-Y: (a)—just after run 5 was complete; (b)—after outgassing the i.r. cell at room temperature; (c)—after heating at 100°C under vacuum; (d, e, f)—after heating at 200°C under vacuum for 4, 10 and 20 hr respectively.

solid of several amino-acids and u.v. visible substances. In the gaseous phase HCN was detected. H₂ could possibly be present but it could not be detected.

The different amino-acids have been identified whereas the u.v. absorbing and fluorescent substances have not yet been determined. Only the presence of adenine was established.

The direct condensation of adenine from HCN has been reported by several authors using different reaction media or energy sources such as heating HCN in aqueous ammonia (Oró and Kimball, 1962; Oró and Kamat, 1961; Matthews and Moser, 1967; Wakamatsu *et al.*, 1966), or irradiating aqueous solutions of hydrogen cyanide (Oró and Kimball, 1963; Oró and Kimball, 1967; Ponnampereuma *et al.*, 1963). Electron irradiation of methane, ammonia and water also has produced adenine (Ponnampereuma *et al.*, 1963).

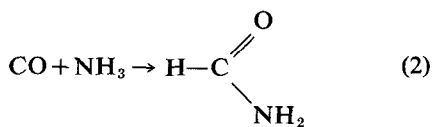
HCN was detected as intermediate product during the synthesis of amino-acids and of purines from simple gases, either submitted to electric discharges (Miller, 1953; 1957), electron irradiation (Palm and Calvin, 1962) and also when an iron meteorite powder (Hayatsu *et al.*, 1968) was used as catalyst.

In the present study, HCN has been obtained by reacting CO and NH₃ in contact with X and Y-sieves, pretreated in a non-oxidizing atmosphere. Two reaction paths, at least, are possible:

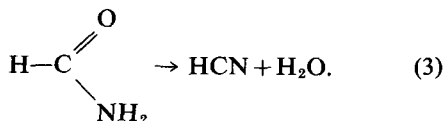
(1) The direct synthesis



(2) The indirect path



followed by



The equilibrium constants vs. temperature of reactions (1) and (2) are shown in Fig. 6.

Since the equilibrium constant of reaction (1), even at 330°C, is not too favorable and since formamide formation is lower at high than at low temperature, the indirect path is perhaps the favored one. It was ascertained that no detectable trace of HCN was formed at 330°C in absence of Ca-Y or Fe-X. However, the catalytic activity

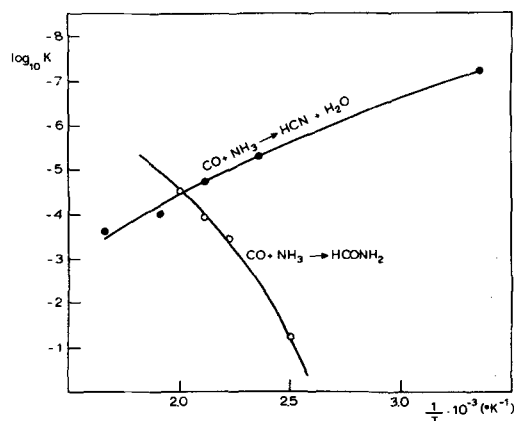


Fig. 6. Equilibrium constants of reaction (1) and (2) (see text).

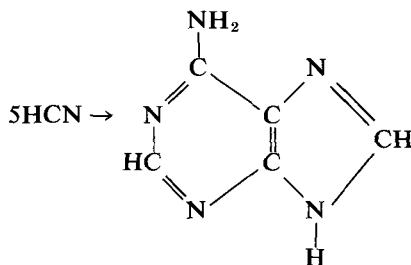
of the Ca- and Fe-sieves in the HCN synthesis is not obvious.

It is known (Perry and Keller, 1956) that the alkaline-earth cations are able to form ammine complexes, such as Ca(NH₃)₆²⁺. If some kind of intermediate results from the addition of NH₃ to the coordination sphere of CaOH⁺ or Ca²⁺, in which NH₃ is strongly polarized, then such a complex may perhaps react with CO and produce formamide, HCN and water, H₂O replacing NH₃ in the coordination sphere. The same picture would hold for the Fe-X sieve.

Angel and Schaffer (1966) have shown that the CO stretching band shifts towards a lower frequency when carbon monoxide interacts with an alkaline-earth sieve and they interpret this shift by assuming an interaction cation-lone pair orbital of CO. This interaction is still more pronounced in the case of iron.

In all these considerations, the acid character of the X and Y sieves in presence of traces of water must be kept in mind.

If the polymerization of cyanhydric acid into adenine can be simply represented as



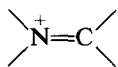
all the intermediate steps involved in such a condensation are not taken into account. In fact the

importance of the dimer, trimer and tetramer forms has been emphasized by several authors (Oró and Kimball, 1962). Ferris and Orgel (1965) observed that the tetramer is the most prominent polymer during the polymerization of HCN, the rate determining steps in the process being the formation of the dimer (Toupance *et al.* 1970). The trimer (or aminomalononitrile) is generally found to be a very reactive form (Sanchez *et al.*, 1967). The hydrolysis of these polymeric forms of HCN generates amino-acids.

Instead of describing various reaction paths leading to various amino-acids, it seems to the authors preferable to adopt a view point somewhat similar to that proposed by Akabori (1957) and supported by Matthews and Moser (1967), i.e. that the synthesis reaction after the formation of HCN leads in one step to a precursor polymer which upon further hydrolysis liberates amino-acids (see Fig. 7).

As suggested in this work by i.r. spectroscopy, such a polymer is likely to be present and its thermal degradation seems to produce more individualized components.

The starting point of the mechanism proposed by Akabori might be considered as an aminocyanocarbene, as suggested by Matthews and Moser (1967). Consequently the difference between the two reaction schemes is perhaps more formal than real. However, the Akabori mechanism requires at the beginning, H₂ and further, free aldehydes. The formation of various amino-acids from the polymer precursor in Matthews' mechanism does not imply this intermediate. Therefore as it has not been possible so far to isolate aldehydes, the right part of Fig. 7 seems preferable. H. G. Viehe (1971) pointed out to the authors the possible formation of an immonium intermediate



because of its high reactivity. Indeed this link is present in the assumed aminocyanocarbene.

All through the block diagram in Fig. 7, HCN is a key reagent. In the early story of the amino-acid synthesis, HCN, NH₃ and aldehydes were already being used by Strecker (1850) as starting reagents.

Jay and Curtius (1894) observed that the reaction of formaldehyde with NH₄CN gives H₂C=N-CH₂-CN which is potentially present in the precursor polymers on the right of Fig. 7.

The aminocyanocarbene is also, as suggested by Oró (cited in Keopian's *Origin of Life*, 1968) a precursor to the adenine synthesis. Moreover in the course of this synthesis, other intermediates may react with guanidine for instance to give other purine bases. As CO₂ is produced at several steps

through decarboxylation reactions, the formation of urea is likely, which, by further reaction with NH₃, leads to guanidine.

Finally, it might be anticipated that the final

hydrolysis process transforming the $\begin{array}{c} \diagup \\ \text{C} = \text{NH} \\ \diagdown \end{array}$ group into carbonyl or the -CN group into carboxyl, could also leach the polymer from the surface. This could insure the formation of coacervates which have been invoked by Oparin and many authors as being a prerequisite to the formation of any biologically significant material.

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Résumé—Cet article a pour but de montrer que les propriétés catalytiques d'un matériau zéolitique peuvent jouer un rôle dans la synthèse de molécules biologiques simples à partir de gaz trouvés couramment dans les atmosphères extraterrestres. Des tamis moléculaires Linde X et Y sous les formes cationiques Ca^{2+} et Fe^{3+} ont été chauffés en présence d'oxyde de carbone et d'ammoniac. Des acides aminés et des substances absorbant dans l'u.v. identifiés par chromatographie sur papier, ont été extraits du solide. HCN, la molécule de base impliquée dans la synthèse de ces substances a été détecté dans la phase gazeuse. On propose, sur la base des résultats infrarouges, que les acides aminés soient les produits d'hydrolyse d'un polymère non défini.

Kurzreferat—In diesem Artikel wird versucht darzulegen, dass die katalytischen Eigenschaften von zeolithartigem Material eine Rolle spielen können bei der Synthese einfacher biologischer Moleküle aus üblicherweise in ausserhalb der Erdatmosphäre gefundenen Gasen. Linde X und Y Molekularsiebe, kationen—ausgetauscht durch Ca^{4+} und Fe^{3+} , wurden erwärmt in der Gegenwart von Kohlenoxyd und Ammoniak. Aus dem Feststoff wurden Aminosäuren und durch Papierchromatographie identifizierte U.V.-absorbierende Substanzen extrahiert. HCN, das grundlegende an des Synthese dieser Stoffe beteiligte Molekül, wurde in der Gasphase aufgefunden. Auf Grund der Ultrarotergebnisse wird angenommen, dass es sich bei den Aminosäuren um Produkte eines nichtdefinierten Polymers handelt.

Резюме—В этой работе делается попытка показать, что каталитические характеристики цеолитного материала могут играть роль в синтезе простых биологических молекул газов обычно находящихся в неземных атмосферах. Молекулярные сита Linde X и Y с катионным обменом Ca^{2+} и Fe^{3+} подогрели в присутствии окиси углерода и аммиака. Вещества, абсорбирующие аминокислоты и U.V., опознанные посредством бумажной хроматографии, экстрагировались из твердого вещества. HCN, основная вовлеченная в синтез этих веществ молекула была замечена в газовой фазе. Инфракрасные результаты приводят к предположению, что аминокислоты являются продуктами гидролиза неопознанного полимера.