MECHANISMS OF AMINO ACID POLYCONDENSATION ON SILICA AND ALUMINA SURFACES

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(Received August 14, 1990)

Abstract. Chemisorption products of bifunctional amino acid vapours on the surface of silica and alumina have been studied by the method of infrared spectroscopy. On the basis of the analysis of spectral data it is supposed that heterogeneous polycondensation of amino acids with formation of peptides proceeds under these conditions. The supposition was confirmed by the study of products of interaction of amino acid vapours with silica and alumina by the method of fast atom bombardment mass-spectrometry. It is established that in contrast to alumina the condensation of amino acids into linear peptides on silica surface proceeds only at presence of at least small amounts of water. The most probable mechanisms of extending of peptide chains are proposed on the basis of obtained experimental data.

1. Introduction

According to Bernal (1951) adsorption and condensation of amino acids into polypeptides could best of all proceed on the surface of inorganic matrixes. Silica and alumina, both in free state and in the form of clay minerals of complex composition, are solid inorganic compounds mostly distributed in the Earth's crust. A lot of model experiments carried out in different laboratories have shown that the formation of peptide bonds proceeds more efficiently on the surface of clays (Brack, 1976; Lahav *et al.*, 1978; White and Erickson, 1980; Lahav and White, 1980; Paecht-Horowitz and Eirich, 1988; Fripiat *et al.*, 1966; Degens and Matheja, 1970) and different forms of silica (Rohlfing and McAlhaney, 1976; Baratova *et al.*, 1970; Visotskii *et al.*, 1967), than in homogeneous systems (solutions). Condensation of amino acid adenylates on clays has been observed (Paecht-Horowitz and Eirich, 1988), but a possibility of prebiotic synthesis of such complex activated amino acid derivatives is an independent problem. At the same time, formation of peptides from individual amino acids on inorganic matrixes may be initiated by physical effects such as high temperature (Rohlfing and McAlhaney, 1976; Visotskii *et al.*, 1967; Fripiat *et al.*, 1966; Degens and Matheja, 1970), temperature and humidity fluctuations (Lahav *et al.*, 1978; White and Erickson, 1980; Lawless and Levi, 1979), and shock waves (Baratova *et al.*, 1970).

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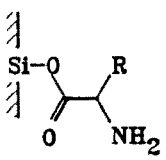
Origins of Life and Evolution of the Biosphere **20**: 483–498, 1990–1991.

Elucidation of the role of silicon and aluminium atoms in the process of activation of amino acids is one of the interesting aspects of simulation of matrix prebiotic synthesis of peptides. They are simultaneously present on the surface of clay minerals, in particular, in a form of surface silanol SiOH and aluminol AlOH groups. Macklin and White (1985) consider that both esters of amino acids with silanol groups and analogous adducts with aluminol groups can act as 'activated intermediates'. Theoretical studies (Collins *et al.*, 1988) have shown that the latter are more stable than the former and can serve as stable nuclei for the growth of long polypeptide chains. Model experiments have shown (Rohlfing and McAlhaney, 1976; Baratova *et al.*, 1970; Visotskii *et al.*, 1967), that silica is capable to catalyze the polycondensation of amino acids, though there are no concrete data on the process mechanism; as for alumina, its capability to initiate formation of peptide bonds has not been experimentally studied as far as we know.

The presence of considerable amounts of water in a reaction mixture is a characteristic feature of all previous model experiments. As a result, it is difficult to study the given systems by the spectral methods, in particular, by the method of infrared spectroscopy which can give useful and detailed information on chemical transformations of amino acids. Besides, the presence of water as one more chemical reagent can initiate competing reactions in the systems under study (for example, hydrolysis), and thus, the elucidation of the mechanisms of heterogeneous polycondensation of amino acids will be very difficult.

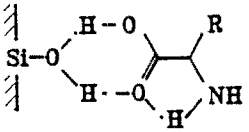
At the same time, a study of reactions proceeding in a two component 'surface-organic compound vapours' system is very convenient from the view point of methodology. Such an experimental approach permits reducing, to a minimum, the number of possible reaction channels and simplifying the study by the spectral methods of processes proceeding in a heterogeneous system. If the organic compound is volatile this approach may be considered trivial. Amino acids, which exist in a condensed phase as zwitterions, are considered non-volatile compounds, that is why, at first glance, the gas-phase procedure of a chemisorption study can not be applied to them. But, as Gross and Grodsky (1955) have established, many amino acids can be sublimed when heated in a vacuum, not only without decomposition and intermolecular condensation, but also without loss of optical activity.

Using this property of amino acids, Groenewegen and Sachtler (1972, 1974) studied the interaction of vaporous glycine, alanine and some other amino acids with the surface of dehydrated pyrogeneous silica (cabosil); they have established that ester-type surface compounds are formed as a result of condensation of carboxylic and silanol groups



(1)

which are characterized by $\nu_{C=0}$ absorption in IR spectra at 1740 cm^{-1}. They have assigned an absorption band at 1670 cm^{-1} to $\nu_{C=0}$ vibrations in hydrogen-bound associations of amino acids with silanol groups



(2)

In the case of glycine, Groenewegen and Sachtler (1972) have not found spectral manifestations of chemical interactions of the given amino acid with silica surface.

The latter finding seemed strange to us as well because of the fact that $\nu_{C=0}$ absorption of hydrogen-bound associations of amino acids with silanol groups was observed by Groenewegen and Sachtler at 1670 cm^{-1}, while $\nu_{C=0}$ absorption of associations of other carboxylic acids is observed about 1720 cm^{-1} (Young, 1969). To find out the mechanism of interaction of amino acids with the surface of silica and alumina we have performed a more detailed investigation. We used the methods of IR spectroscopy and fast atom bombardment (FAB) mass-spectrometry to analyse products of interaction of bifunctional α-amino acid vapours (glycine, alanine, valine, leucine, isoleucine, phenylalanine, and methionine) with dehydrated surfaces of silica and alumina.

2. Experimental

The quartz cell that was described by Nikitin *et al.* (1956) was used for adsorption studies in a vacuum (Figure 1). Oxides in a form of thin compacted tablets were evacuated at 10^{-4} –10^{-2} Torr for 1 hr at 700 °C. Amino acid (about 10 mg) was placed into heated zone of the vacuum cell, close to the oxide tablet. The temperature was such that the sublimation could proceed with sufficiently high speed (10–20 min) and, at the same time, that the interval between the given temperature and melting point of amino acid was not less than 30 °C (such a limit provides thermal stability of molecules in a gas-phase). IR spectra of tablets (UR-20 spectrophotometer, Karl Zeiss, Jena, Germany; the range of 1300–1900 cm^{-1}) were recorded after condensation of the excess amino acid in the cold zone of the cell.

When reproducing the sublimation experiment in a minipreparative scale (Figure 2) about 50 mg of amino acid and 500 mg of oxide (control experiment, sublimation of amino acid without oxide) were placed into the quartz tube. The temperature of preliminary dehydration of oxides varied from 200 to 700 °C.

To identify products of amino acid condensation we have used the method of FAB mass-spectrometry. This method, due to the 'softness' of this way of ionization, guarantees the absence of further chemical transformations of biomolecules in the course of registration of mass-spectra. The analyses were performed on MX 1310 mass-spectrometer (Nauchpribor, Orel, USSR); the range of measurements, 100–

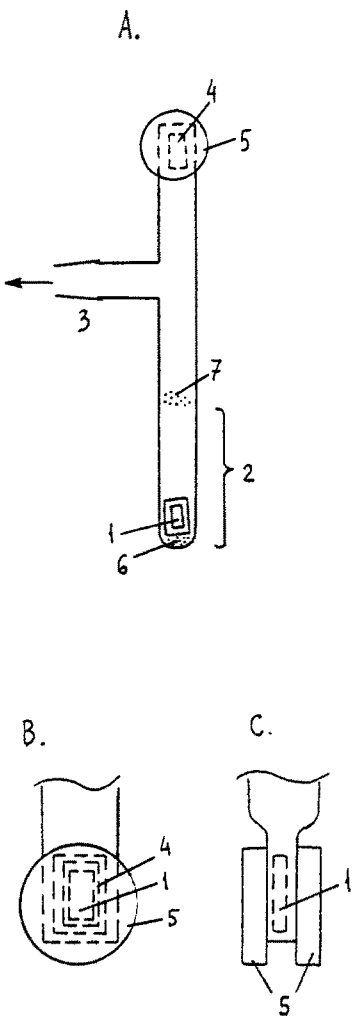


Fig. 1. The quartz cell for IR studies of amino acid chemisorption on silica and alumina. (A) position during chemisorption. (B) position during IR measurements. (C) side-view. (1) silica or alumina in a form of thin compacted tablet in a fused quartz holder; (2) heated zone; (3) joint through which tablet and amino acid are deposited into the cell; arrow, to vacuum source; (4) window; (5) KRS-5 glass (IR transparent); (6) amino acid before and, (7) after sublimation.

600 atomic mass units, a.m.u. Samples (sublimates in the case of silica; alumina with chemisorbed species) in a form of suspensions in glycerol were placed to the target, then the target was placed into the ion source. Energy of bombarding argon atoms was 3.5 keV; intensity of bombarding beam about 1 μA; angle of incidence to the target, 70° to the normal.

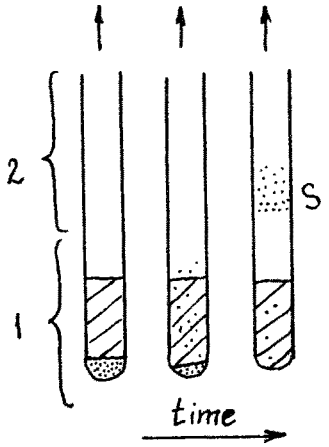


Fig. 2. Scheme of sublimation experiment in a mini-preparative scale. Heated (1) and cold (2) zone of the quartz tube; ☹: amino acid; ▨: silica or alumina (control experiment, sublimation in absence of oxides); arrow, to vacuum source (10^{-1} – 10^{-2} Torr); S, sublimate.

3. Results and Discussion

Interaction of amino acid vapours with silica

As is seen from Figure 3, all amino acids under study are chemisorbed on silica, the IR spectra of tablets being similar in all cases. Presence in the spectra of not two (Groenewegen and Sachtler, 1974) but three $\nu_{C=0}$ absorption bands at 1670, 1720, and 1760 cm^{-1} are seen clearly. The last band is attributed to ester linkage (Young, 1969) (these surface compounds play the role of 'activated intermediates' in the processes of heterogeneous polycondensation of amino acids into peptides (White *et al.*, 1982; Macklin and White, 1985)). In our opinion, the band at 1720 cm^{-1} corresponds to $\nu_{C=0}$ absorption in hydrogen-bound associations but not at 1670 cm^{-1} (Groenewegen and Sachtler, 1972, 1974). Certainly, one can suppose, that besides the type 2 associations there exist any other ones, but it is doubtful that the difference in $\nu_{C=0}$ frequences for different hydrogen-bound associations should be 50 cm^{-1}. It is more likely that the amino acids condense to form short peptides which are characterized by $\nu_{C=0}$ absorption in the region of 1650 cm^{-1} (the band 'amide I') (Bellamy, 1954). The absence of δ_{NH} band ('amide II') in the region of 1550 cm^{-1} does not contradict this proposal since this frequency is characteristic for amides with trans-arrangement of amide bond only. In the case of cis-arrangement the absorption 'amide II' is much lower in frequency and it can not be distinguished because of interaction with δ_{CH} (Dementyeva *et al.*, 1969). In particular, this is observed for the cyclic glycine dipeptide, diketopiperazine (Newman and Badger, 1951). Upon heating the tablets further, the intensities of all absorption bands gradually decrease to almost complete restoration of IR spectra of initial dehydrated silica samples. This fact proves the supposition about further

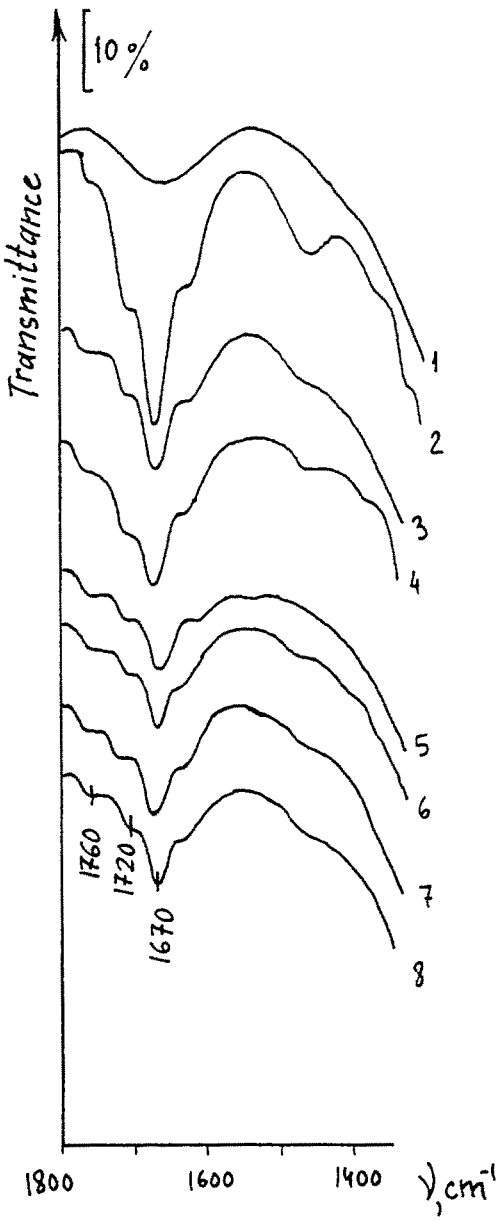


Fig. 3. IR spectra of silica tablets (1) after gas-phase treatment by phenylalanine at 250 °C (2), methionine at 250 °C (3), glycine at 260 °C (4), alanine at 220 °C (5), valine at 250 °C (6), isoleucine at 250 °C (7), and leucine at 230 °C (8). Pyrogeneous silica (specific surface area about 300 $m^2\ g^{-1}$) in a form of compacted thin tablets (8–10 mg cm^{-2}) was preliminary dehydrated in vacuum at 700 °C.

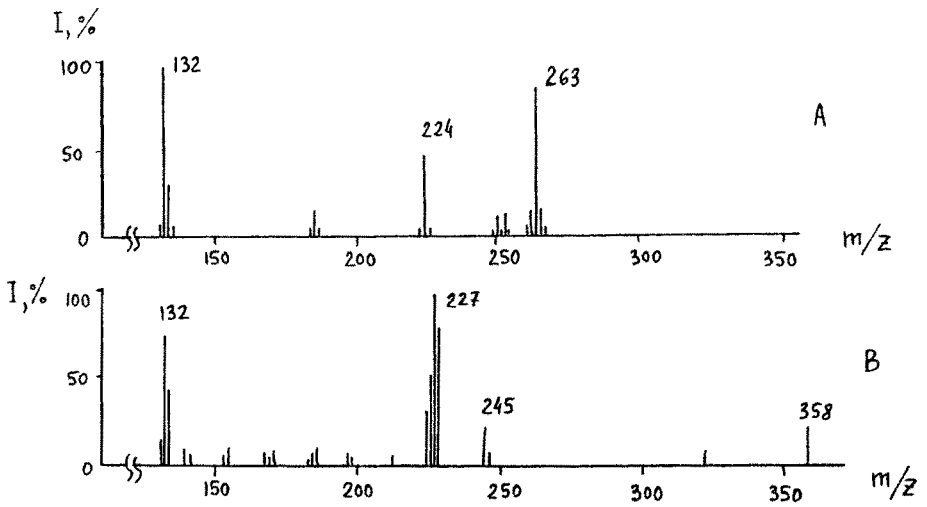


Fig. 4. FAB mass-spectra of leucine sublimated at 220 °C in absence (A) and in presence (B) of silica. Peak assignment (m/z, a.m.u.): Leu · H^+ (132), Leu · G · H^+ (224), cyclo-Leu_2 · H^+ (227), Leu_2 · H^+ (245), 2Leu · H^+ (263), Leu_3 · H^+ (358); G, molecules of glycerol in cluster ions.

chemical transformations of surface esters. That is why Groenewegen and Sachtler (1972) have not found interaction of glycine with cabosil surface: after the 20-hour chemisorption experiment neither chemisorbed glycine nor products of its transformations remained on the tablet.

To prove directly intermolecular condensation of amino acids in the presence of silica we have performed the sublimation experiment on a micropreparative scale

TABLE I

Mass numbers (a.m.u.; in brackets, relative intensity, I, %) of molecular and cluster ions in FAB mass-spectra of products of amino acid sublimation in presence (SiO_2) and in absence (control) of silica, preliminary dehydrated at 200 °C.

Glycine		Leucine		Phenylalanine		Proline		Peak reference[b]
Control 230°[a]	SiO_2 220°	Control 220°	SiO_2 220°	Control 220°	SiO_2 220°	Control 200°	SiO_2 190°	
76(100)	76(20)	132(100)	132(80)	166(100)	166(10)	116(100)	116(100)	A · H^+
–	115(100)	–	227(100)	–	295(100)	195(5)	195(60)	C · H^+
–	133(90)	–	245(20)	–	312(<5)	–	–	D · H^+
–	190(30)	–	358(20)	–	–	–	–	T · H^+
168(30)	–	224(50)	–	258(30)	–	208(60)	208(40)	A · G · H^+
–	–	263(90)	–	331(40)	331(10)	231(80)	–	2A · H^+
–	–	–	–	–	–	300(20)	300(20)	A · 2G · H^+
–	–	–	–	–	–	310(10)	–	A · C · H^+)

[a] Temperature of sublimation.

[b] Abbreviations: A, amino acid; D, dipeptide; T, tripeptide; C, diketopiperazine; G, glycerol.

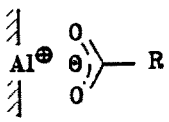
(Figure 2), and the sublimates condensed in the tube cold zone have been studied by the method of FAB mass-spectrometry. In the mass-spectra (Figure 4, Table I), as it was expected, we have registered ions of protonated molecules of initial amino acids and products of their heterogeneous condensation (short linear peptides and diketopiperazines), in some cases in the form of clusters with glycerol molecules. In the control experiment (amino acids sublimed at the same temperatures or even at much higher ones, but in the absence of silica) products of condensation were not revealed in FAB mass-spectra.

It should be emphasized that besides initial amino acids, only diketopiperazines, i.e. completely dehydrated dipeptides, were found in samples sublimed in the presence of completely dehydrated (at 800 °C) silica. Thus, the presence of at least monolayer hydrate cover on the silica surface is necessary for formation of linear peptides (temperature of preliminary treatment of silica below 400 °C).

It is possible that amino acids can be condensed into longer linear peptides on partially dehydrated silica, but peaks of corresponding ions were not found in the mass-spectra.

Interaction of amino acid vapours with alumina

The results of our IR spectroscopic studies of the interaction of amino acid vapours with dehydrated alumina agree with results of theoretical study (Collins *et al.*, 1988). As it is evident from comparison of IR spectra of silica tablets (Figure 3) and alumina ones (Figure 5) with chemisorbed amino acids, intensities of absorption bands in the latter case are much higher than in the former one; moreover, they almost do not decrease in the process of long-term thermo-vacuum treatment. Here, three absorption bands are distinguished. The band at 1615–1630 cm^{-1} corresponds to $\nu^{as}_{CO_2^-}$ vibrations of ionized carboxylic groups in salt compounds with surface atoms of aluminium (Greenler, 1962; Hasegawa and Low, 1969).



(3)

These compounds are characterized by high stability and, in contrast, to ester linkage of silanol groups, they begin to form upon contact of alumina with water solutions of amino acids (glycine, see Figure 5, curve 3). The absorption bands at 1680–1695 and 1510–1550 cm^{-1} correspond $\nu_{C=0}$ vibrations ('amide I') and δ_{NH} ('amide II') respectively in linear peptides (in the case of proline, Figure 5, curve 5, containing one hydrogen atom of the amino group, the band 'amide II' is absent). Thus, if upon contact of amino acid vapours with completely dehydrated silica, surface condensation proceeds only into diketopiperazines, desorbed in the course of thermo-vacuum treatment, linear peptides strongly bound with the surface are formed on completely dehydrated alumina.

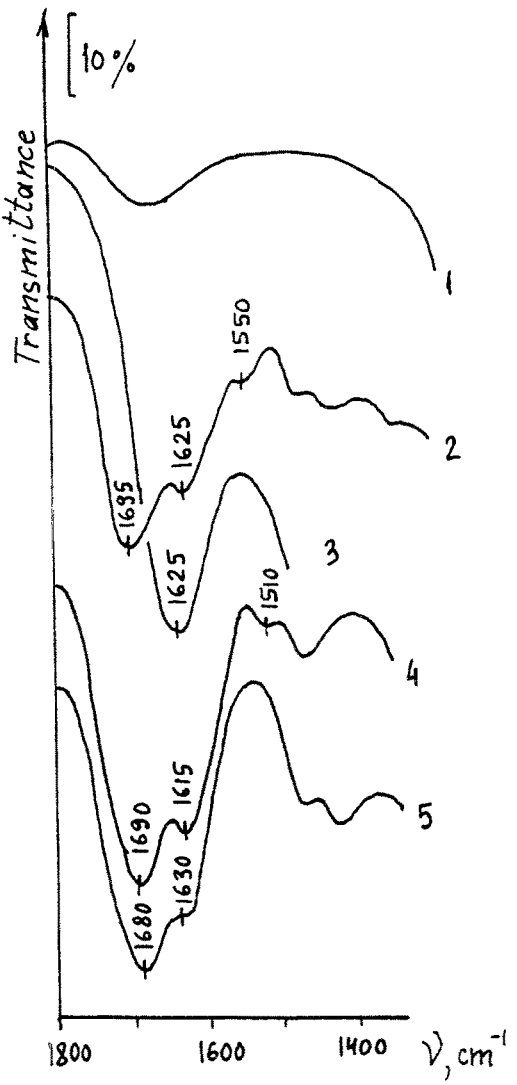


Fig. 5. IR spectra of alumina (1), after treatment by vapours of glycine at 210 °C (2), phenylalanine at 220 °C (4), proline at 200 °C (5), after glycine impregnation from water solution (3). Highly dispersed alumina (specific surface area 140 $m^2\ g^{-1}$) in a form of compacted tablets preliminary dehydrated in vacuum at 700 °C (1, 2, 4, and 5); 3, in a form of suspension in nujol.

Investigation of the products formed from amino acid vapours on alumina (mini-preparative experiment, Figure 2) by the method of FAB mass-spectrometry has confirmed the formation of linear condensation products with a length of up to four amino acid residues (Figure 6). Thus, in the case of glycine we have found di-, tri-, and tetraglycine linear peptides (which were absent in the control experiment, glycine sublimed in absence of alumina). Treatment of alumina by equimolar mixture of glycine and alanine resulted in formation on alumina surface of peptides containing

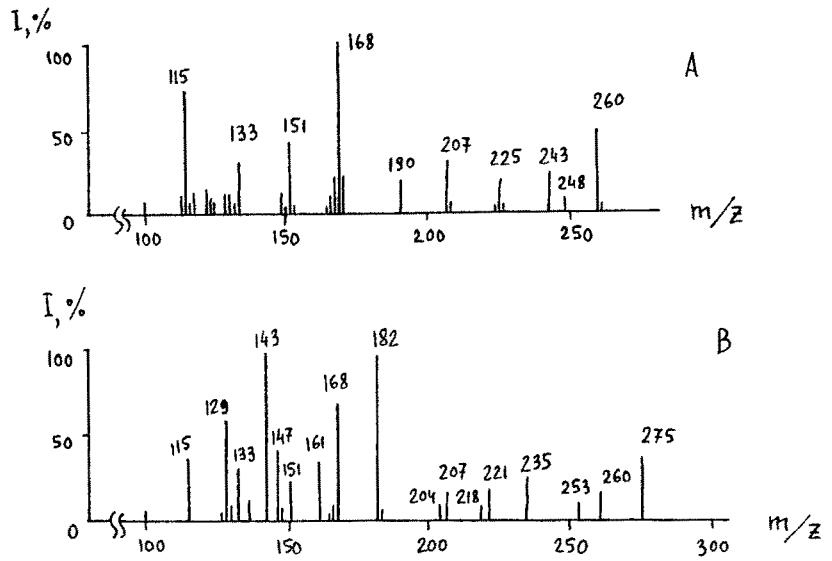


Fig. 6. FAB mass-spectra of alumina samples after treatment at 210 °C by glycine vapours (A) and equimolar mixture of glycine and alanine (B). Peak assignment (m/z, a.m.u.): cyclo-$Gly_2 \cdot H^+$ (115), cyclo-Gly-Ala $\cdot H^+$ (129), $Gly_2 \cdot H^+$ (133), cyclo-$Ala_2 \cdot H^+$ (143), Gly-Ala $\cdot H^+$ (147), 2Gly $\cdot H^+$ (151), $Ala_2 \cdot H^+$ (161), Gly $\cdot$ G $\cdot H^+$ (168), Ala $\cdot$ G $\cdot H^+$ (182), $Gly_3 \cdot H^+$ (190), Gly_2–Ala $\cdot H^+$ (204), cyclo-$Gly_2 \cdot$ G $\cdot H^+$ (207), Gly-$Ala_2 \cdot H^+$ (218), cyclo-Gly-Ala $\cdot$ G $\cdot H^+$ (221), $Gly_2 \cdot$ G $\cdot H^+$ (225), cyclo-$Ala_2 \cdot$ G $\cdot H^+$ (235), 2Gly $\cdot$ G $\cdot H^+$ (243), $Gly_4 \cdot H^+$ (248), $Ala_2 \cdot$ G $\cdot H^+$ (253), Gly $\cdot$ 2G $\cdot H^+$ (260), Gly_2–$Ala_2 \cdot H^+$ (275). G, glycerol molecules in cluster ions. Peptides containing both Gly and Ala are of unestablished sequence.

residues of both amino acids (Gly-Ala, Gly-Ala_2, Gly_2-Ala, Gly_2-Ala_2 of unestablished sequence were found). Presence in the mass-spectra of intensive peaks corresponding to diketopiperazines (cyclo-Gly_2, cyclo-Ala_2, cyclo-Gly-Ala) proved a bit unexpected. This may be explained in two ways: either thermally and hydrolytically stable surface salt-linkages can play the role of 'activated intermediates', or there exists a path to formation of diketopiperazines which is not related to the catalytical activity of alumina surface.

Reactivity of ester and salt-linkages

To compare the capability of ester and salt-linkages to form amide bonds under action of amines we have chosen the model system, 'carboxylic acid (benzoic or stearic) chemisorbed on surface (silica or alumina) and octadecylamine'. As in the previous case, the investigations were carried out using the gas-phase procedure.

IR spectra of chemisorbed benzoic acid are presented in Figure 7. The ester with silanol group is characterized by $\nu_{C=0}$ absorption at 1750 cm^{-1}, surface aluminium benzoate – by $\nu^{as}_{CO_2^-}$ absorption at 1620 cm^{-1}. Treatment of the former by octadecylamine vapours at 100 °C results in almost complete disappearance of the ester band and appearance of intensive bands 'amide I' at 1665 cm^{-1} and 'amide

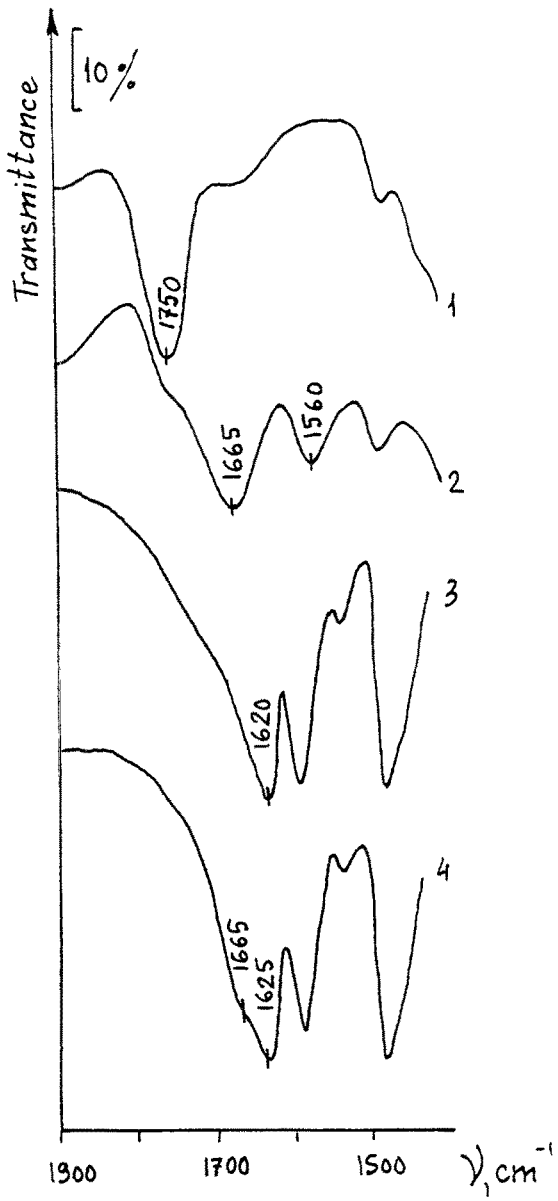
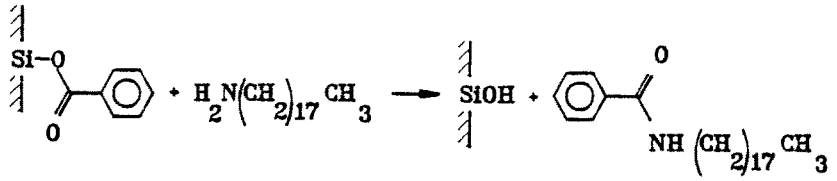


Fig. 7. IR spectra of benzoic acid chemisorbed at 200 °C on silica (1) and alumina (3), after treatment by octadecylamine vapours at 100 °C for 0.5 hr (2) and at 200 °C for 0.5 hr (4), respectively.

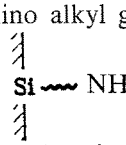
II' at 1560 cm^{-1} (Figure 7, curve 2). These changes point to the formation of octadecylamide of benzoic acid according to following scheme:

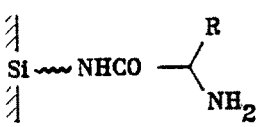


and, thus, evidence for the conception of ester 'activated intermediates'.

In the second case (alumina) no changes were observed in the IR spectrum after treatment by octadecylamine at 100 °C (only after elevating the temperature of treatment to 200 °C was the appearance of low-intensity shoulder at 1665 cm^{-1}, Figure 7, curve 4). Similar results were obtained in the case of chemisorbed stearic acid. These data demonstrate that, in contrast to ester linkages, salt-linkages can not be considered unconditionally as 'activated intermediates' in the processes of heterogeneous polycondensation of amino acids. Thus it is difficult to explain peptide formation from amino acids on the surface of pure alumina.

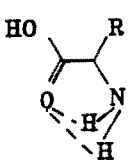
THE SECOND WAY OF PEPTIDE CHAIN GROWTH

Recently it was established that amino alkyl groups chemically bonded to silica surfaces relatively easily form amides  upon interaction with vapours of monofunctional carboxylic acids and amino acids (Basiuk and Chuiko, 1989, 1990). Formation of amide bonds in both cases proceeds rather quickly at temperatures above 150 °C without activation of carboxylic groups and use of condensing reagents. Intermolecular condensation of vaporous amino acids is not observed under these conditions. But after the first amino acid residue is chemisorbed on amino alkyl silica with formation of amide



(4)

the α-amino group can be condensed with the next molecule of amino acid with formation of dipeptide, then of tripeptide, etc. Such a heterogeneous polycondensation was observed in the case of glycine (Basiuk and Chuiko, 1990). Apparently there exist large differences in the reactivity of amino groups involved in intramolecular hydrogen bonds



and amino groups in surface compounds $\equiv X - Y - NH_2$, where X = Si; Y = $(CH_2)_n$, $(CH_2)_nNHCOCHR$ (4), OCOCHR (1); or X = Al; Y = $^-$OCOCHR (3) (Sheina *et al.*, 1988). Then, one can suppose that the alternative (in respect to the conception of 'activated intermediates' by White *et al.*) way of amino acid activation, by inorganic oxides, consists of the removal of intramolecular association via binding carboxylic group of amino acid molecule with surface functional groups; as a result, the α-amino group acquires a capability to condense with the carboxylic group of the next amino acid molecules.

Taking into account both possibilities, the mechanisms of amino acid activation and peptide formation on the surface of clay minerals, silica and alumina can be presented as in Figure 8. As it is seen, the A mechanism of growth is more general than the B mechanism, since it can be realized on the surface of all mentioned inorganic oxides.

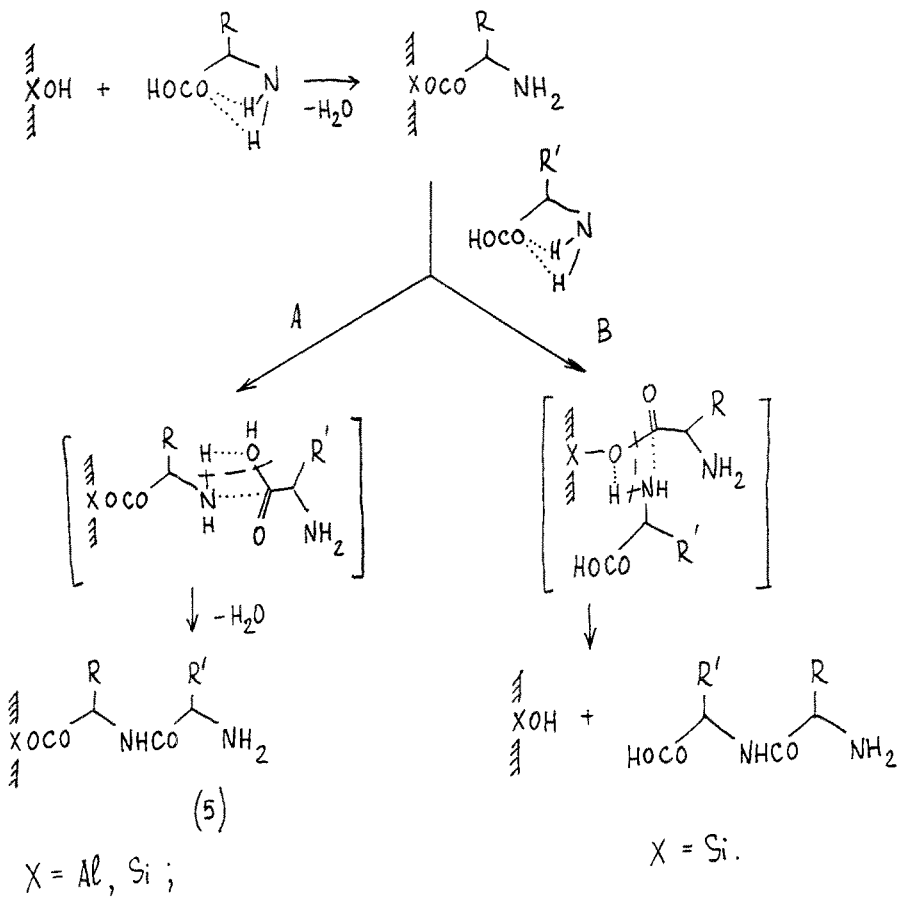
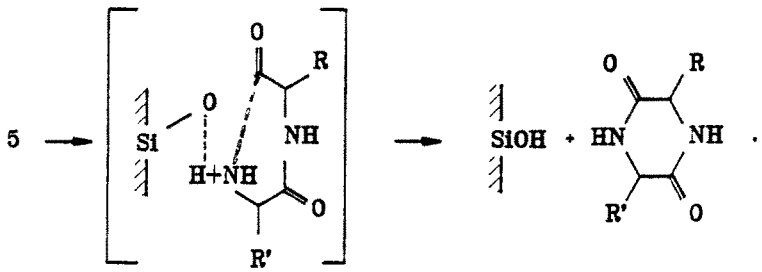


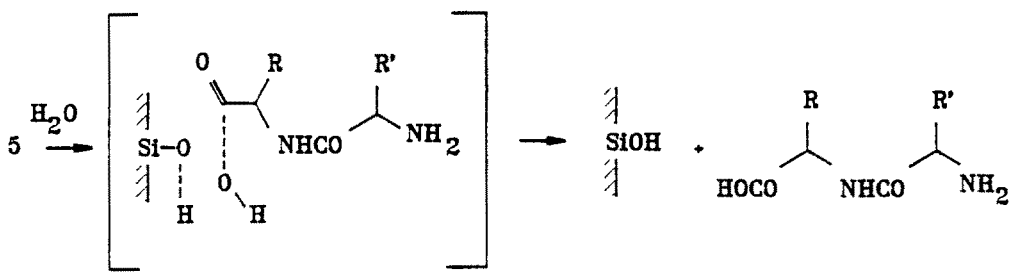
Fig. 8. Schematic representation of two most probable mechanisms of peptide chain growth on the surfaces of silica and alumina.

DIKETOPIPERAZINES

The mechanisms represented in Figure 8 can also explain formation of diketopiperazines with participation of silanol groups. Dipeptide 5 bound with the surface, already formed via the A mechanism of growth, is cyclized according to the B mechanism:



On a completely dehydrated surface of silica the cyclization proceeds with maximum yield. If there is some amount of water in the system, the way formation of linear peptides as a result of hydrolysis of their esters with silanol groups can occur is shown below:



As was noted, the B route is not observed on pure alumina. But under these conditions diketopiperazines are formed in large amounts. We think that they are degradation products resulting from splitting of the N-terminal dipeptide residue with its simultaneous cyclization. For example, in the case of tripeptide:

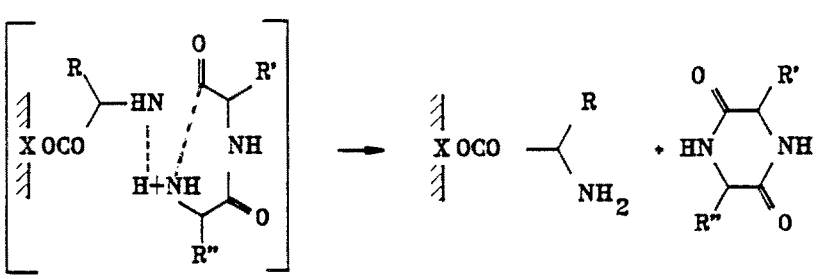


TABLE II

Relative intensities of peaks (I, %) in FAB mass-spectra of products of transformations of Gly-Val on silica and alumina and without them (control).

Compound	I, %		
	Control	SiO_2	Al_2O_3
Gly	4	15	3
Val	25	100	100
Cyclo-Gly-Val	25	100	65
Gly-Val[a]	100	100	100
Val_2	4	5	8
Gly_2-Val	3	7	9
Cyclo-$(Gly\text{-}Val)_2$	1	11	4
$(Gly\text{-}Val)_2$	3	7	4
$(Gly\text{-}Val)_3$	1	5	5

[a] The most intensive peak.

Such reactions are observed in homogeneous medium, in overheated (under pressure) water solutions (White, 1984; Moir and Crawford, 1988).

One should allow for a possibility of manifestation of enzyme-like ('peptidase') activity of peptide chains (White and Erickson, 1980; Dose, 1974) as well as assume that oxide matrixes (as catalysts in general) can accelerate not only in direct reaction (condensation) but also in the reverse (hydrolysis). To evaluate these possibilities we subjected to thermal treatment (120 °C, 5 hr) two peptides, diglycyl-glycine and glycyl-valine adsorbed from water solution to silica and alumina (10 mg of peptide to 50 mg of oxide) and in the absence of oxides (control experiment). Formation of peptides $(Gly\text{-}Val)_2$, $(Gly\text{-}Val)_3$, cyclo-Gly-Val, and cyclo-$(Gly\text{-}Val)_2$ (products of condensation of initial Gly-Val), as well as glycine, valine, Val-Val and Gly_2-Val (products of competing reactions of hydrolysis and condensation) were observed for glycyl-valine (Table II) in all three cases. As it is evident from a comparison of peak intensities in FAB mass-spectra (Table II), all these processes proceed more intensively on the surface of oxide matrixes. Apparently silica and alumina also catalyze reactions of peptide hydrolysis. Products of destruction (glycine, Gly_2, and cyclo-Gly_2) are also found in all three cases for diglycyl-glycine. As regards to the product of chain doubling, Gly_6, it was found only in the systems with oxides; formation of cyclo-Gly_6 being also observed in presence of silica (cyclization probably proceeds in the same way as in the case of diketopiperazines, via the B mechanism).

4. Conclusion

The obtained experimental data permits the following conclusions. Two mechanisms of peptide chain growth were readily detected on the silica surface, but only one could be detected on the alumina surface. Condensation of amino acids into linear

peptides on the silica surface is possible only in the presence of at least small amounts of water (adsorbed monolayer). Linear peptides are formed in detectable amounts on the alumina surface in the absence of water. The competitive destructive processes (hydrolysis, formation of diketopiperazines) proceed parallel with heterogeneous polycondensation of amino acids, but accumulation of peptides in the system occurs under such rigid conditions as temperatures of about 200 °C and absence of water as a separate phase. Thus, formation of peptides via the matrix polycondensation of amino acids in prebiotic era could proceed long before the beginning of the world ocean formation (water condensation on the planet surface). Allowing for the fact that amino acids can form both in processes of volcanic activity (Podkletnov and Markhinin, 1981) and under space conditions (Orò *et al.*, 1971), the region of prebiotic synthesis of peptides could be almost anywhere.

References

Baratova, L. A., Goldanskii, V. I., Kosigin, M. J., and Yampolskii, P. A.: 1970, *Biokhimiya* **35**, 1216 (Russian).

Basiuk, V. A. and Chuiko, A. A.: 1989, *Dokl. Akad. Nauk SSSR* **309**, 381 (Russian).

Basiuk, V. A. and Chuiko, A. A.: 1990, *Zh. Prikl. Spektrosk.* **52**, 935 (Russian).

Bellamy, L. J.: 1954, *The Infrared Spectra of Complex Molecules*, John Wiley and Sons, N.Y.

Bernal, J. D.: 1951, *The Physical Basis of Life*, Routledge and Kegan Paul, London.

Brack, A.: 1976, *Clay Miner.* **11**, 117.

Collins, J. R., Loew, G. H., Luke, B. T., and White, D. H.: 1988, *Orig. Life* **18**, 107.

Degens, E. T. and Matheja, J.: 1970, in A. P. Kimball and J. Oró, (eds.), *Prebiotic and Biochemical Evolution*, North Holland Publishing Company, pp. 39–69.

Dementyeva, L. A., Iogansen, A. V., and Kurkchi, G. A.: 1969, *Zh. Prikl. Spektrosk.* **10**, 625 (Russian).

Dose, K.: 1974, *Orig. Life* **5**, 239.

Fripiat, J. J., Cloos, P., Calicis, B., and Makay, K.: 1966, *Proc. Intern. Clay Conf. Jerusalem* **1**, 233.

Greenler, R. G.: 1962, *J. Chem. Phys.* **37**, 2094.

Groenewegen, J. A. and Sachtler, W. M. H.: 1972, *J. Catal.* **27**, 369.

Groenewegen, J. A. and Sachtler, W. M. H.: 1974, *J. Catal.* **33**, 176.

Gross, D. and Grodsky, G.: 1955, *J. Amer. Chem. Soc.* **77**, 1678.

Hasegawa, M. and Low, M. J. D.: 1969, *J. Colloid and Interface Sci.* **30**, 378.

Lahav, N., White, D. and Chang, S.: 1978, *Science* **201**, 67.

Lahav, N. and White, D. H.: 1980, *J. Mol. Evol.* **16**, 11.

Lawless, J. and Levi, N.: 1979, *J. Mol. Evol.* **13**, 281.

Macklin, J. W. and White, D. H.: 1985, *Spectrochim. Acta* **41A**, 851.

Moir, M. E. and Crawford, R. J.: 1988, *Can. J. Chem.* **66**, 2903.

Newman, R. and Badger, R. M.: 1951, *J. Chem. Phys.* **19**, 1147.

Nikitin, V. A., Sidorov, A. N. and Karyakin, A. V.: 1956, *Zh. Fiz. Khim.* **30**, 117 (Russian).

Oró, J., Gilbert, J., Lichtenstein, H., Wikstrom, S., and Flory, D. A.: 1971, *Nature* **230**, 105.

Paecht-Horowitz, M. and Eirich, F. R.: 1988, *Orig. Life* **18**, 359.

Podkletnov, N. E. and Markhinin, E. K.: 1981, *Orig. Life* **11**, 303.

Rohlfing, D. L. and McAlhaney, W. W.: 1976, *BioSystems* **8**, 139.

Sheina, G. G., Radchenko, E. D., Ivanov, A. Yu., Stepanyan, S. G. and Blagoi, Yu. P.: 1988, *Zh. Fis. Khim.* **62**, 985 (Russian).

Visotskii, Z. Z., Danilov, V. I., and Strelko, V. V.: 1967, *Usp. Sovr. Biol.* **63**, 362 (Russian).

White, D. H. and Erickson, J. C.: 1980, *J. Mol. Evol.* **16**, 279.

White, D. H., Kennedy, R. M., and Macklin, J. W.: 1982, *Abs Pap. ACS* **183**, 28.

White, R. H.: 1984, *Nature* **310**, 430.

Young, R. P.: 1969, *Can. J. Chem.* **47**, 2237.