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PREBIOTIC CHEMISTRY

# Adsorption and Polymerization of Amino Acids on Mineral Surfaces: A Review

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**Abstract** The present paper offers a review of recent (post-1980) work on amino acid adsorption and thermal reactivity on oxide and sulfide minerals. This review is performed in the general frame of evaluating Bernal's hypothesis of prebiotic polymerization in the adsorbed state, but written from a surface scientist's point of view. After a general discussion of the thermodynamics of the problem and exactly what effects surfaces should have to make adsorbed-state polymerization a viable scenario, we examine some practical difficulties in experimental design and their bearing on the conclusions that can be drawn from extant works, including the relevance of the various available characterization techniques. We then present the state of the art concerning the mechanisms of the interactions of amino acids with mineral surfaces, including results from prebiotic chemistry-oriented studies, but also from several different fields of application, and discuss the likely consequences for adsorption selectivities. Finally, we briefly summarize the data concerning thermally activated amide bond formation of adsorbed amino acids without activating agents. The reality of the phenomenon is established beyond any doubt, but our understanding of its mechanism and therefore of its prebiotic potential is very fragmentary. The review concludes with a discussion of future work needed to fill the most conspicuous gaps in our knowledge of amino acids/mineral surfaces systems and their reactivity.

**Keywords** Amino acids · Adsorption · Surface polymerization · Oxide minerals · Bernal's hypothesis

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## Introduction

In the sequence of organizational events leading to the emergence of life, many competing scenarios have been proposed to explain the appearance of small biomolecules such as amino acids or nucleotides. The following step up the organizational ladder is the polymerization of these small molecules to give biopolymers such as proteins (or RNA, respectively).

This represents another formidable problem apparently intractable by solution chemistry, for reasons explained in "Why Biopolymers Formation is Forbidden in Water Solution" below. Recently, among nine basic standing questions regarding the origin of life asked at the Erice international course on complexity, the following one was put forward: "How to Make Prebiotically Long Hetero-Peptides or Hetero-Nucleotides?" (Stano and Luisi 2007).

Among the solutions that have been proposed, one may cite salt-induced peptide formation (SIPF: Rode et al. 1991; Eder and Rode 1994; Rode 1999), hydrothermal synthesis (Imai et al. 1999), impact polymerization (Lyons and Vasavada 1999; Blank et al. 2001), polymerization by coupling to metaphosphate hydrolysis (Yamagata and Inomata 1998), and polymerization in the adsorbed phase which is the topic of this review—several solutions may be combined in one scenario, e.g. surface polymerization+SIPF (Le Son et al. 1998).

Over 50 years ago, it has been proposed by Bernal (Bernal 1951) that the biomolecules polymerization step actually involved reactions on mineral surfaces, a mechanism later dubbed "polymerization on the rocks" (Orgel 1998; Liu and Orgel 1998). For a long time, little experimental investigations were undertaken to test this hypothesis. Now many relevant studies are appearing in the scientific literature, either in the context of prebiotic chemistry or in very different fields. We think that it is time to systematize knowledge gained in this way, and to underline remaining problems.

## Scope of this Review and State of the Art

Here we concentrate on the adsorption and reactivity of amino acids and "small peptides," and their further reactivity, on surfaces resembling minerals that were likely present on the early earth, mostly silicates, oxides, and sulfides. This excludes the adsorption on reduced metal surfaces for which much information is available, but which have a very different reactivity from oxide surfaces and are not very likely candidates for prebiotic chemistry; this particular field was recently reviewed by (Barlow and Raval 2003).

We have also chosen not to treat the adsorption and polymerization of nucleic acids. Although this problem is very similar to the case of amino acids, the molecules concerned are more complex, and the smaller number of relevant studies does not, in our opinion, allow to reach generally significant conclusions.

There was an initial flurry of activity on surface-aided amino acids polymerization in the 1970s, mostly concerned with clay minerals. This early literature has been reviewed by (Lahav and White 1980; Rao et al. 1980) and (Ponnamperuma et al. 1982).

The field has apparently not progressed much in the 1980s. A renewed interest is apparent starting in the mid-1990's, (in part triggered by Wächtershäuser's ideas of "two-dimensional life": Wächtershäuser 1988) with more systematic studies, some broadening of the range of surfaces studied, and the beginning of application of new techniques to the problem (molecular modeling, adsorption on singe crystal surfaces). This interest is not only driven by the relevance for prebiotic chemistry, but also by potential applications in quite different fields such as biocompatibility and biomaterials.

A recent review on peptides and the origin of life is that of (Rode 1999), but the effect of adsorption (mostly on clay minerals) is not the main focus of this work, except as an adjuvant to SIPF scenarios. Much information concerning the adsorption of amino acids on silica, especially thermodynamic data, can be found in (Basiuk 2002); the review by Zaia (2004) also constitutes an interesting complement to the present one.

## General Problematics

### Why Biopolymers Formation is Forbidden in Water Solution

It is a recurrent theme of prebiotic chemistry literature to wonder how likely it is that the random polymerization of monomers could have resulted in a functional polymer or a functional system. Widely divergent estimates have been put forward, depending on the initial assumptions: thus, Hoyle and Wickramasinghe (quoted in Shapiro 1986) required the random assembly of a set of 2,000 proteins having an average length of 200 AAs, comparable in complexity to a small bacterium, and came up with the discouragingly small probability of $10^{-40,000}$ for spontaneous assembly, even allowing for some structural variability. They compared this figure to an estimated number of random trials of the prebiotic earth that could have been carried out in the primordial ocean: at most $2.5\times10^{51}$. At the other extreme, Trifonov (2006) supposed that the formation of a peptide as small as 20 AAs was enough to start chemical evolution and went on to calculate that "a small truckload of chemicals" (370 kg of an amino acids mixture) was enough to achieve this.

However, these estimates most often only consider the question of amino acids polymerization selectivity: they implicitly suppose that each encounter between two amino acids results in peptide bond formation, and calculate the probability that the obtained sequence is the right one.

In fact, peptide bond formation itself is thermodynamically unfavorable in water solution under reasonable conditions. The thermodynamic problem can be stated easily. If we write the dimerization reaction as:

$$X_{\text{solution}} + X_{\text{solution}} = X - X_{\text{solution}} + \text{H}_2\text{O} \quad (1)$$

(where $X$ is a generic amino acid monomer), then thermodynamic data indicate that the free enthalpy of dimerization $\Delta_{\text{dimer}}G°$ is positive by several kJ $\text{mol}^{-1}$ (e.g. +14.25 kJ $\text{mol}^{-1}$ at RT if $X$=Gly: Shock 1992). Therefore dimerization is indeed disfavored; for instance, at equilibrium, an initially 0.5 mol $\text{l}^{-1}$ solution of glycine at RT will have produced only $1.5*10^{-5}$ mol $\text{l}^{-1}$ of dimer. Further polymerization events are also unfavorable, which is illustrated on Fig. 1 by the successive polymers in solution lying further and further up on the G° scale. Amino acids polymerization in solution will only yield ridiculously small amounts of polypeptides, as a rough calculation will show. If we take an average value of +10.45 kJ $\text{mol}^{-1}$ for the free enthalpy of formation of further peptide bonds (Martin 1998), we find that the equilibrium concentration in the same solution of a 14-mer is $2.6\times10^{-30}$ mol $\text{l}^{-1}$, and that of a 18-mer is $1.49\times10^{-38}$ mol $\text{l}^{-1}$, or about one molecule per hundred cubic kilometers of highly concentrated primordial soup, which is not a bright prospect to start metabolism. Very similar considerations have been presented recently by Brack (2007) with the same conclusion.

Note that the figures above are obtained for homogeneous glycine polymerization. In a mixture of amino acids, the selectivity factor will further decrease the probability of meeting the

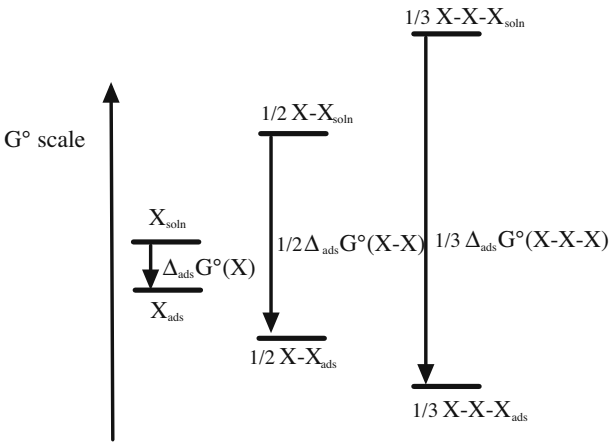



**Fig. 1** A sketch of the thermodynamic parameters (free enthalpies) regarding the polymerization of an amino acid X, in solution and in a hypothetical adsorbed state

"right" polymer at equilibrium. But even without taking into account the selectivity factor, the emergence of polypeptides by polymerization in solution is not a viable option. A similar argument could be made for nucleic acids polymerization to RNA: no matter what biopolymer initiated the rise to complexity, its emergence is no trivial matter.

## Do We Need a Catalyst?

Often, popular presentations of the problem of prebiotic polymer formation cursorily invoke "a catalytic effect" of mineral surfaces to explain its occurrence on the early earth. This is misleading: the discussion above has shown that the main problem lies in the thermodynamics of the polymerization reaction, not its kinetics.

Of course every chemical problem has a kinetic as well as a thermodynamic dimension, and the kinetics of peptide bond formation and hydrolysis are slow, with times in the order of several centuries being reported at neutral pH (Radzicka and Wolfenden 1996). Now a few centuries do not seem too long on the scale of geological time; thus, the kinetics dimension is not the first question in the problem of bioplymers formation. Catalysis may have helped but it is not required—and it may be a double-edged sword because what speeds up polymerization also speeds up the reverse reaction of polymer degradation (see Zamaraev et al. 1997, for an application of this general principle to amino acids chemistry, where silicate catalysts increased the speed of hydrolysis of Gly–Gly to Gly). At any rate, it is worth repeating that no amount of catalysis can revert the thermodynamics of a chemical reaction: what we need first and foremost is to find (hopefully realistic) conditions in which the thermodynamics of polymerization becomes favorable.

## Polymerization During Adsorption

If we suppose that the adsorption of monomers reverses the polymerization thermodynamics to make it allowed, we have to wonder why: does there exist an "adsorbed phase" in which the thermodynamic functions of the intervening molecules are different from the bulk solution (there are indeed reasons to believe that a water solution in close contact to an oxide surface is very different from the bulk, see e.g. Danielewicz-Ferchmin and Ferchmin 2004), or is adsorption only the beginning of a more complicated process, that includes further steps such as drying? Let us consider the first option.

de Duve and Miller (1991) have pointed out that for dimerization to become thermodynamically favorable in the adsorbed state, the free energy of adsorption of the dimer must be more negative than that of two monomers by an amount of at least 20 kJ $mol^{-1}$. Formally, they wrote the dimerization in solution as

$$X_{\text{solution}} + X_{\text{solution}} = X - X_{\text{solution}} \tag{2}$$

and its counterpart in the "adsorbed state" as

$$X_{\text{adsorbed}} + X_{\text{adsorbed}} = X - X_{\text{adsorbed}} \tag{3}$$

They postulated that reaction 3 could be favorable even though reaction 2 is unfavorable; the corresponding energetic situation is sketched in Fig. 1 (more will be said in "Or Polymerization upon Drying" regarding the difference between Eqs. 1 and 2).

Furthermore, for polymerization in the adsorbed state to go on and form higher oligomers, the *increment* in adsorption energy for each added amino acid in the polymer must be higher and higher as the polymer chain grows [$(X)_{3\ \text{ads}}$ must be more stabilized than $(X)_{2\ \text{ads}}+X_{\text{ads}}$]. The longer a polymer becomes, the tighter it is adsorbed to the surface. Then higher polymers would essentially be irreversibly adsorbed.

Orgel et al. are comfortable with the idea (Hill et al. 1998). On the other hand, results on polypeptide adsorption (Gerstner et al. 1994) indicate that the contribution to the adsorption free enthalpy of each additional unit bound to the surface is approximately constant as the chain grows, which would result in less and less efficient surface polymerization. Whatever the specifics, the irreversible adsorption of surface-formed polymers would result in a paradox that may be summarized as follows: if the initial steps of life really occurred on surfaces, how then did life escape surfaces at a later stage? This has lead some authors to speculate that the first protocells were indeed bounded by mineral walls such as may be found in the porosity of silicate minerals (Parsons et al. 1998; Smith 1998). Alternatively, as we shall see in the following paragraph, polymerization could occur during a later drying step rather than immediately after adsorption; in that case, there is no need for adsorbed polymers to be highly stabilized energetically relative to polymers in solution, and therefore desorption of biopolymers need not be so unfavorable. In fact, there are not very many precise data on the thermodynamics of amino acids and peptide adsorption, with the notable exception of adsorption on silica where many free energies of adsorption were estimated by Basiuk (Basiuk and Gromovoy 1996; Basiuk 1998). For monomers, they are almost always positive (0 to + 4 kJ $mol^{-1}$). A compensation effect was observed between $\Delta_{\text{ads}}H°$ and $\Delta_{\text{ads}}S°$ (Basiuk and Gromovoy 1996): while the adsorption of most amino acids was exothermic, the entropic contribution was unfavorable.

Several dipeptides had slightly positive to slightly negative free energies of adsorption ($\Delta_{\text{ads}}G°$ of −1 to +1,4 kJ $mol^{-1}$: Basiuk and Gromovoy 1994; Basiuk 1998). Thus, it would seem that adsorption alone could indeed favor polymerization, although maybe not to the extent wished by de Duve and Miller (1991). Another relevant piece of work is the adsorption of $(Gly)_2$, $(Gly)_3$, and $(Gly)_4$ on montmorillonite clays by Kalra et al. (2003). The $\Delta_{\text{ads}}G°$ was positive (unfavorable) for $(Gly)_2$ (+0.9 to +1.1 kJ $mol^{-1}$), close to zero for $(Gly)_3$ and slightly negative for $(Gly)_4$ (−0.6 to to −0.8 kJ $mol^{-1}$). Again, we have the right trend, but the slope seems too small. More data can be found in the review by Basiuk (2002), confirming the trend at least for adsorption on silica.

The situation gets thermodynamically more complicated when the adsorbed amino acids bear a net non-zero charge (e.g. negative for Glu or Asp, positive for Lys, Arg…). In this case, a strong non-ideality of their behavior in the adsorbed state is expected due to

electrostatic repulsion between adsorbed amino acids. To be sure, this repulsion may be partly offset by their common attraction to a surface of opposite charge (*vide infra*, "Electrostatic Adsorption") and the energetics could in principle be treated by standard colloid chemistry models. Such theoretical treatments have not been undertaken so far, in spite of their importance to check intuitive ideas often put forward in prebiotic chemistry accounts: e.g., that the surface concentration of monomers by electrostatic adsorption is enough to overcome the energetic barrier to polymerization (Danchin 1990).

Even if amino acid polymerization is indeed favored in the adsorbed state, its kinetics may be quite slow. To check whether it occurs at this stage, it would be necessary to perform experiments on suspensions of oxides in amino acid solutions with very long equilibration times and without thermal activation. This does not seem to have been done. To summarize, it is not impossible that adsorption alone may have caused amino acid polymerization, but there is not a shred of positive evidence so far.

## Or Polymerization upon Drying?

The argument developed in the preceding paragraph is incomplete. It is based on writing the reaction as $X+X=X-X$, as in Eq. 2, which neglects the formation of water, as opposed to the complete formulation in Eq. 1.This is valid in a dilute solution, where the activity of water $a_{H_2O}$ is almost constant. If that holds, the true equilibrium constant for dimerization $K = \frac{a_{X-X} a_{H_2O}}{(a_X)^2}$ may be replaced by $K' = \frac{K}{a_{H_2O}} = \frac{a_{X-X}}{(a_X)^2}$, which formed the basis for de Duve and Miller's (1991) reasoning.

On the other hand, if $a_{H_2O}$ is variable, decreasing it will automatically increase the equilibrium dimer/monomer ratio; and when $a_{H_2O}$ tends towards zero, polymerization reactions tend towards completion. Thus, polymerization reactions can be made favorable if they are coupled with a physical process that decreases $a_{H_2O}$. This can contribute to rationalize the effect of ion strength in the salt-induced peptide formation, but of course the simplest way to decrease $a_{H_2O}$ is to dry the system by external heating. In a prebiotic scenario, this can be achieved by exposure to the sun; it is not necessary that high temperatures be reached—they would speed up the kinetics of course, but it is the elimination of water, not the temperature, that solves the thermochemical problem.

Of course, one can wonder if mineral surfaces are necessary at all in that case; and indeed intriguing results have been reported on the bulk drying of drops of amino acid solutions (Viedma 2000; Napier and Yin 2007). But if one considers the probable amino acid concentrations in the primordial ocean, it seems likely that after drying the molecules would not form bulk precipitates, but indeed be subject to the thermochemical and kinetical influence of the surfaces on which they were left to dry.

## Amino Acid Polymerization by Surfaces Together with Activating Agents

Protein chemists essentially synthesize peptides in the same way as the cell machinery does: by coupling the thermodynamically unfavorable peptide bond formation with a thermodynamically favorable reaction. They use sacrificial "coupling agents" or activators, such as 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide (EDC) and 1,1′-carbonyldiimidazole (CDI). Of course such molecules are not expected to have been present in significant amounts on the prebiotic earth. Commeyras et al. (2002) have proposed an elaborate scheme of oligopeptide formation using a more likely coupling agent, the cyanate ion $NCO^-$. However, their scheme, dubbed the "primary pump," also necessitates a physical process, solution concentration by evaporation, and thus it constitutes a combined scenario involving several effects.

Orgel and coworkers did also study the polymerization of amino acids on mineral surfaces, using activators—carbodiimides (Hill et al. 1998; Liu and Orgel 1998) or carbonyldiimidazole (Ferris et al. 1996; the same strategy was used for nucleotide polymerization). Lee and Frank (2003) polymerized *N*-carboxyanhydrides (NCA) of various amino acids, which constitute a well-known activated form, on Si wafers: in the same way, Yanagawa et al. (1990) polymerized preformed amides of several amino acids in the presence of kaolinite (Ito et al. 1990). Bertrand et al. (2001) obtained oligopeptides up to seven amino acids long by polymerizing leucine thioethylesters in the presence of CdS. These studies still fall within the scope of the present review, but mostly because of the theoretical and experimental questions of polymerization kinetics that they address: as regards the thermodynamic problem of polymerization, it is solved in a different way than by adsorption and thermal activation.

Other cases are less clear. Naka et al. (2007) studied the oligomerization of phenylalanine in the presence of the carbodiimide EDAC at 0°C. At some pH values, the % yield of poly(Phe) was increased by a factor of two or three, all other things being equal, when $Fe(OH)_3$ sols were added. The effect invoked was "molecular assembly of the amino acid onto the iron (III) hydroxide matrix," which seems in fact to be a thermodynamic effect based on concentration increase in the "adsorbed phase."

A special case of coupling would be one in which the thermodynamically favorable reaction would be a transformation of the surface: in the case of iron sulfides, which can partake in redox reactions, Wächtershäuser et al. hypothesized that the formation of pyrite ($FeS_2$) from FeS and $H_2S$ can provide the driving force for the activation of the carboxylic acid group (through reductive acetylation of amino acids with mercaptoacetic acid $HSCH_2COOH$), which is "converted to a species that reacts readily with amines" (Keller et al. 1994). This interesting idea has not been tested. For the possible coupling with strained siloxane rings opening on the surface of silica, see "Specific Adsorption by Covalent Bond Formation."

## Some Questions of Practical Experiment Design

### Adsorption from Solution vs. Adsorption from the Gas Phase

The colloid chemistry community, and most biologists, naturally favor adsorption from aqueous solutions. This is certainly the most relevant situation for prebiotic chemistry. On the other hand, physicists specializing in surface science tend to favor deposition directly from the gas phase. This is partly due to cultural reasons (the urge to simplify the system by avoiding the interference of water), but also to technical demands of the characterization methods employed, especially for adsorption on single crystals.

In spite of the apparently unrealistic character of adsorption from the gas phase,[1] results obtained in this way can be very significant, either to clearly evidence a particular adsorption mode, or to mimic what happens when the water activity is decreased by drying. However, it must be kept in mind that when the question has been studied the presence of water did indeed interfere strongly with amino acid adsorption modes.

[1] Unrealistic at least for the early earth; but they may be highly relevant in other contexts, such as interstellar dust grains.

Tables 1 and 2 list the studies published on amino acid adsorption on oxides from the aqueous phase and from the gas phase, respectively. It can be seen that the former are considerably more numerous, with the exception of Basiuk & al.'s early work on amino acids CVD (Chemical Vapour Deposition) on powders: the few studies on single crystals are quite recent.

## To Wash or not to Wash

If we want to study amino acids adsorbed on surfaces in the dry state (cf. "Or Polymerization upon Drying"), we must separate the solid phase from the solution with which it has been equilibrated, by filtration or centrifugation; but the solid phase will physically retain a more or less important amount of this solution, still containing amino acids that do not interact with the surface. Upon drying, the latter will either be forced to enter a different type of interaction with the surface, or they will precipitate separately (Meng et al. 2004). Thus, the solid sample obtained will contain different chemical forms of the amino acid, probably having different reactivities (there exists a close analogy with the situation in supported catalysts preparation by transition metals deposition from water solution; Lambert and Che 2001).

If one or several washing steps are applied to obviate this difficulty, on the other hand, the adsorption equilibrium will be perturbed. In other systems (such as transition metals on oxide surfaces), it is possible to minimize desorption by using fast washing procedures, because desorption is an activated process and therefore slow at room temperature. In the case of amino acids, the activation energy for desorption is expected to be smaller (especially if they are adsorbed by the formation of H-bonded surface adducts, *vide infra* "Specific Adsorption by Hydrogen Bonding"), so that the application of washing steps runs the risk of desorbing most of the molecules that one wants to study in the first place.

There is no satisfactory way out of this conundrum. From a prebiotic point of view, scenarios without a washing step are probably more realistic, but they make the characterization of the adsorbed species more difficult.

## Techniques for Characterization of the Adsorption Mechanism and the State of Adsorbed Amino Acids

### *Macroscopic Data for Amino Acid Adsorption on Oxide Powders (Divided Matter)*

Perhaps the least demanding technically are studies of the bulk adsorbed amounts of amino acids in different experimental conditions. First, adsorption isotherms (amount of amino acid adsorbed as a function of equilibrium concentration in the solution) may be measured. In simple situations, they can provide equilibrium constants for adsorption (which give access to the $\Delta_{ads}G°$), and saturation coverages—unfortunately, the latter are often given per unit mass of the solid adsorbent (mmol $g^{-1}$), while it would be much more informative to give them per unit exposed surface (mmol $m^{-2}$).

In the high concentration domain, adsorption may be estimated from the decrease in solution concentration, measured by chromatography or spectrophotometry. Adsorption from very dilute solutions may be studied by radiotracer experiments. Even though such conditions are probably quite relevant for prebiotic chemistry, these studies are not frequent (for an example of $^{14}C$ labeling, see Matrajt and Blanot 2004).

Realizing several adsorption isotherms at different temperatures can in principle give access to the enthalpic and entropic part of the $\Delta_{ads}G°$ (Wijntje et al. 2006).

**Table 1** Experimental studies mainly concerned with amino acid adsorption from an aqueous phase onto oxide minerals

| Oxide mineral | Amino acid | Main techniques used | Reference |
|---|---|---|---|
| $SiO_2$, $Al_2O_3$, mica, kaolin | Pyroglutamic acid | IR | Macklin and White 1985 |
| $SiO_2$ | dipeptides, cyclic and linear | Free energies of adsorption | Basiuk and Gromovoy 1993a |
| $SiO_2$ | dipeptides, cyclic and linear | Free energies of adsorption | Basiuk and Gromovoy 1994 |
| $SiO_2$ | Ala, Asn, Asp, Cys, Gln, Glu, Gly, Ile, Leu, Met, Phe, Pro, Ser, Tyr, Thr, Trp, Val | Free energies of adsorption | Basiuk and Gromovoy 1996 |
| $SiO_2$ | Ala, Asn, Asp, Cys, Gln, Glu, Gly, Ser, Tyr, Thr, Trp, Val | Free energies of adsorption | Basiuk 1998 |
| $SiO_2$ | Gly | IR, macroscopic data | Meng et al. 2004 |
| $SiO_2$ | Arg, His, Lys | macroscopic modeling | Vlasova and Golovkova 2004 |
| $SiO_2$ | Gly, Lys | IR, macroscopic data, molecular modeling | Stievano et al. 2007 |
| $SiO_2$ (quartz), albite, calcite monocrystals | Ala, Asp, Glu, Gly, Leu, Lys, Tyr | AFM (atomic force microscopy) | Churchill et al. 2004 |
| Modified $SiO_2$ | Gly, Leu, His, Lys | Adsorption isotherms | Kunota et al. 1996 |
| Glass, hydrophilic and hydrophobic | Leu, Ser | Isotopic labeling | Alaeddine and Nygren 1996 |
| $SiO_2$, coadsorption with $Cu^{2+}$ | Ala, Leu, Phe, Trp, Tyr, Val | Macroscopic data, adsorption isotherms | Vlasova 2005 |
| $SiO_2$, $Al_2O_3$ Low-Ss powders | His, Trp | Adsorption isotherms, macroscopic modeling | Palit and Moulik 2001 |
| MCM-41 (mesoporous $SiO_2$) | $(Ala)_4$ | Deuterium NMR | Pizzanelli et al. 2005 |
| MCM-41 (mesoporous $SiO_2$) | Lys | Adsorption isotherms, macroscopic modeling | O'Connor et al. 2006 |
| SBA-15 (mesoporous $SiO_2$) mesoporous carbon | His | Adsorption isotherms | Vinu et al. 2006 |
| $Al_2O_3$, with acidic or basic treatments | Glu | Macroscopic data | Moitra et al. 1984 |
| $Al_2O_3$, with acidic or basic treatments | Asp | Macroscopic data | Moitra et al. 1984 |
| $Al_2O_3$, with acidic or basic treatments | Gly, Ser | Macroscopic data | Moitra et al. 1984 |
| $Al(OH)_3$, AlOOH | Gly | EPR | McBride 1985 |
| $Al_2O_3$, with acidic or basic treatments | Arg, His | Macroscopic data | Moitra et al. 1989 |
| $Al_2O_3$ | Gly | Macroscopic data, TG | El Shafei and Philip 1995 |
| $Al_2O_3$ | Glu | IR, macroscopic data | Guo et al. 2006 |
| γ and α-$Al_2O_3$ | Ala | IR | Garcia et al. 2007 |
| $TiO_2$ | Arg, Lys | Adsorption isotherms | Okazaki et al. 1981 |
| $TiO_2$, graphite, $Al_2O_3$ | Gly | XPS | Lundström and Salaneck 1985 |

**Table 1** (continued)

| Oxide mineral | Amino acid | Main techniques used | Reference |
|---|---|---|---|
| $TiO_2$ | Asp | XPS, macroscopic modeling | Giacomelli et al. 1995 |
| $TiO_2$ | Lys | IR | Roddick-Lanzilotta et al. 1998 |
| $TiO_2$ | Lys, Poly(Lys) | IR | Roddick-Lanzilotta and McQuillan 1999 |
| $TiO_2$ | Gly | TPD | Lausmaa et al. 1999 |
| $TiO_2$ | Asp, Glu | IR | Roddick-Lanzilotta and McQuillan 2000 |
| Ferrihydrite (Fe oxyhydroxide) | Gly, Ala, Val, non-biological AAs | $^{14}C$ labeling | Matrajt and Blanot 2004 |
| $Fe(OH)_3$ | Phe | Macroscopic data | Naka et al. 2007 |
| HAP (hydroxyapatite) | His, Met, Trp | | El Shafei and Moussa 2001 |
| HAP | Ser | Adsorption isotherms, zeta potential | Spanos et al. 2001 |
| Zeolites (ZSM5, ZSM11, Y, β) | Glu, Leu Lys, Phe, | Adsorption isotherms, macroscopic data | Munsch et al. 2001 |
| Zeolite ZSM5 | Ala, Phe, Trp, Tyr | Adsorption isotherms and selectivities | Titus et al. 2003 |
| Zeolite β | Arg, Glu, Lys, Phe | Adsorption isotherms, macroscopic information | Krohn and Tsapatsis 2005 |
| Zeolite Y | Gly, $(Gly)_3$ | Adsorption isotherms, macroscopic information | Wijntje et al. 2006 |
| Zeolites X, Y and β | Arg, Phe | Macroscopic (adsorption isotherms, pH dependence) | Krohn and Tsapatsis 2006 |
| Cu-Zeolite Y | His | UV, IR, EPR, XAS | Mesu et al. 2006 |
| $SiO_2$, montmorillonite, illite | Ala, Asn, Asp, Cys, Glu, Gly, His, Ile, Leu, Met, Phe, Pro, Ser, Thr, Trp, Tyr, Val | Free energies of adsorption | Basiuk et al. 1994 |
| Montmorillonite clay | Ala, Gly | Adsorption isotherms | Kalra et al. 2000 |
| Montmorillonite clay | $(Gly)_2$, $(Gly)_3$, $(Gly)_4$ Gly–Ala | Adsorption isotherms | Kalra et al. 2003 |
| Cd-montmorillonite clay | Gly | NMR ($^{13}C$ and $^{111}Cd$) | Di Leo 2000 |
| Cu-saponite clay | His, Lys | EPR, UV | Fu et al. 1996 |
| Bentonite, kaolinite | Ala, Asp, Cys, Gln, His, Lys, Met | Macroscopic information, XRD | Benetoli et al. 2007 |
| Kaolinite | Asp | Adsorption isotherms | Ikhsan et al. 2004 |
| Kaolinite | Gly | IR, TG | Meng et al. 2007 |
| LDH (layered double hydroxides) | Phe | Adsorption isotherms and kinetics, macroscopic information | Aisawa et al. 2006 |
| LDH | Glu | $^{13}C$ NMR, TG | Reinholdt and Kirkpatrick 2006 |

The list is limited to biological L-α-amino acids although in some cases abiotic AAs were studied as well. "Macroscopic data" denote such information as adsorption dependence on pH, ion strength, etc. "Macroscopic modeling": quantitative fitting of adsorption isotherms and other macroscopic data.

**Table 2** Studies mainly concerned with amino acid adsorption from the gas phase onto oxide minerals

| Oxide mineral | Amino acid | Main techniques used | Reference |
|---|---|---|---|
| $SiO_2$ | Ala, Gly, Ile, Leu, Met, Phe, Val | IR | Basyuk 1990 |
| $SiO_2$ | Val, Gly, Ala, leu, Ile, Pro, Phe, Met, Thr, Trp | Analysis of organic products after desorption, condensation and analysis of gaseous products | Basiuk and Gromovoy 1993b |
| $SiO_2$ | $(Gly)_2$, Gly–Ala, Gly–Leu, Gly–Val, Ala–Ala, Val–Val | condensation and analysis of gaseous products | Basiuk and Gromovoy 1993c |
| $SiO_2$ | $(Gly)_2$, Ala–Ala, Leu–Leu, Val–Val, Pro–Pro | condensation and analysis of gaseous products | Basiuk et al. 1992 |
| $Al_2O_3$ (film on NiAl single crystal) | Gly | XPS, TPD, EXAFS | Tzvetkov et al. 2004 |
| $TiO_2$ single crystal, (110) face | Gly | UPS | Soria et al. 1999 |
| $TiO_2$ single crystal, (001) face | Pro | XPS, TPD | Fleming and Idriss 2004 |
| $TiO_2$ single crystal, (110) face | Gly | STM | Qiu and Barteau 2007 |

Analysis of adsorption isotherms as a function of pH may yield precise information on the nature and stoichiometry of adsorbed amino acid/surface complexes using the models of colloid chemistry. Such data were obtained by Ikhsan et al. (2004) (Vlasova and Golovkova 2004—see "Specific Adsorption by Hydrogen Bonding" for a discussion) and Krohn and Tsapatsis (2005, 2006) for amino acid monomers, and by Wijntje et al. (2006) for triglycine.

Adsorption may also be studied as a function of ion strength (I): in the case of electrostatic adsorption ("Electrostatic Adsorption"), increasing I will cause competitive ion exchange and therefore decrease adsorption (Wijntje et al. 2006). If a covalent bond is formed ("Specific Adsorption by Covalent Bond Formation"), no influence of I is expected (Hayes et al. 1988; Giacomelli et al. 1995). More complicated adsorption mechanisms may also be revealed by their dependence on I (Krohn and Tsapatsis 2006).

Dynamic methods (study of partition coefficients between the solid and liquid phase in chromatographic experiments) may also provide independent estimates of the thermodynamic adsorption parameters (Basiuk 1998). It might be instructive to compare estimates of $\Delta_{ads}G°$ obtained on the same material by static and dynamic methods: this has not been done yet.

Finally, powder XRD may provide information on the amino acid/matrix interaction in one particular case, that of layered materials (clays, LDHs), where amino acid intercalation results in an expansion of the unit cell (Siffert and Naidja 1992; Benetoli et al. 2007). This technique may be considered under the "macroscopic" heading since it depends on structural periodicity.

*Spectroscopic Data on Oxide Powders*

In situ spectroscopic data during the adsorption process (i.e., data obtained in the presence of the adsorbing solution) have been so far limited to IR in the ATR mode (Roddick-Lanzilotta et al. 1998; Roddick-Lanzilotta and McQuillan 2000). Of course, vibrational spectroscopy is easily applied to amino acids adsorbed on dry powders (Basyuk 1990; Basiuk et al. 1991). Most oxide materials have a transmission window in the range of CO

and $NH_x$ vibrations, so that vibrational spectroscopy reveals the acid-base speciation of the adsorbed amino acid (e.g. presence of COOH vibrators for the cationic form of amino acids), and sometimes finer structural detail (coordination to surface atoms, specific pattern of H-bonding: Benaziz et al. 2001; Lomenech et al. 2005; Garcia et al. 2007). Later on, during thermal activation, the formation of the amide linkage is very conspicuous in IR (Meng et al. 2004).

$^{13}C$ solid-state NMR has much potential, especially if isotopically enriched amino acids are used (Di Leo 2000; Reinholdt and Kirkpatrick 2006; Stievano et al. 2007). The same remark can be made for $^{15}N$ NMR.

UV-visible spectroscopy, fluorescence methods, Raman and XAS spectroscopy could also be helpful.

It should be underlined that both macroscopic and spectroscopic approaches to adsorption on powders are easiest to carry out when the surface area of the adsorbing oxide is as high as possible.

*Single Crystal Studies*

Studies of the adsorption of amino acids on oxide single crystals have only begun to appear recently, and they are limited to $TiO_2$, or thin films of $Al_2O_3$ on conducting crystals. They can be very informative because ordered two-dimensional periodical adsorbate structures can be formed on such substrates, and characterized by the techniques of single-crystal surface chemistry such as STM (Qiu and Barteau 2007); additional information may be gleaned from UPS-XPS, TPD-SM, etc. (Fleming and Idriss 2004; Tzvetkov et al. 2004). As we said in "Adsorption from Solution vs. Adsorption from the Gas Phase," single crystal studies are generally concerned with adsorption from the gas phase, but this limitation could be overcome.

*Molecular Modeling*

In-depth molecular modeling studies of amino acid adsorption are also quite recent. There were some early attempts to model glycine on clay edges (Collins et al. 1988), and alanine on silica (West and Hench 1994), but technical progresses have made molecular modeling investigations more relevant lately.

In the last three years, several papers have appeared using density functional and hybrid methods on surfaces represented by clusters (Lomenech et al. 2005; Rimola et al. 2006b; Costa et al. 2007; Rimola et al. 2007; Stievano et al. 2007) or periodic structures (Rimola et al. 2006a; Nair et al. 2007). Molecular dynamics methods are beginning to be introduced in order to study the first steps of adsorbed amino acid reactivity (Pollet et al. 2006).

Evaluating the energy profile along the successive steps of the peptide bond formation among adsorbed amino acids, or amino acid analogues, is the declared purpose of several studies (Rimola et al. 2007; Nair et al. 2007).

The success of molecular modeling methods will depend on their ability to correctly predict the values of chemical observables, such as IR vibration frequencies or NMR chemical shifts of adsorbed amino acids. Also, the estimation of Fukui functions constitute an intuitive, but fundamentally well-grounded way to predict reactivity changes of adsorbed species (Pollet et al. 2006).

So far, as can be seen in Table 3, the range of amino acids studied remains limited, with most studies being done on glycine, because of the additional complexity introduced by modeling the side chain.

**Table 3** Mostly theoretical studies (molecular modeling) of amino acid adsorption and/or amide formation reactivity on mineral surfaces

| Oxide or sulfide mineral | Amino acid | Reference |
|---|---|---|
| $SiO_2$ | Ala | Hench and West 1994 |
| $SiO_2$ | Lys | Gambino et al. 2004 |
| $SiO_2$ | Gly | Lomenech et al. 2005 |
| $SiO_2$, silico-aluminas | Gly, "truncated" | Rimola et al. 2005 |
| $SiO_2$ | Lys | Gambino et al. 2006 |
| $SiO_2$ | Gly | Rimola et al. 2006b |
| $SiO_2$, silico-aluminas | Gly | Rimola et al. 2007 |
| $SiO_2$ | Gly | Costa et al. 2007 |
| $SiO_2$ | Gly | Stievano et al. 2007 |
| $TiO_2$ | Cys, Gly, Met, Ser | Langel and Menken 2003 |
| Clays (clay edges) | Gly | Collins et al. 1988 |
| Clay (interlayer) | Model Ala peptide | Yu et al. 2001 |
| Pyrite | Gly | Boehme and Marx 2003 |
| Pyrite | Gly | Pollet et al. 2006 |

## Thermal Activation; Drying and Rewetting Cycles

The simplest way of investigating the reactivity of adsorbed amino acids upon thermal activation (cf. "Or Polymerization upon Drying") would be through a single heating at a controlled temperature, but many studies use more complicated procedures.

One can imagine that after drying of adsorbed amino acids, a further wetting episode (by rain, or exposure to tides) could desorb some of the formed polypeptides, giving a metastable polypeptide solution.

The idea of working in "fluctuating environments" in this context dates back to the work of Lahav et al. (1978) It was meant to simulate in the lab natural periodic variations of the experimental conditions that may have occurred on the prebiotic earth, such as daily fluctuations of temperature and seasonal fluctuations of humidity: similar procedures are also often applied in geochemistry to simulate the natural weathering of primary minerals. Typically, a "WDTF" (wetting-drying and temperature fluctuation, or simply "WD") cycle includes drying of the oxide/amino acid suspension, heating to 80–95°C for up to one day, and resuspending the dry powder in water; this cycle is repeated *n* times prior to analysis of the organic fraction. Recently, Muller and Schulze-Makuch (2006) have proposed a thermodynamic analysis showing how the application of macroscopic cycles, including wetting-and-drying cycles, might drive a chemical reaction that would be endergonic in isolation. The details need elaboration, but this seems to be the right conceptual framework to study complex processes involving macroscopic steps.

## Direct Study of Thermal Reactivity

Peptide formation upon thermal activation can be directly observed by calorimetry or DTA, and also by simple thermogravimetry since the amino acids condensation results in the emission of water molecules to the gas phase. In principle, DTA or calorimetry could allow accurate measurements of the reaction enthalpy, which could then be compared to the

corresponding value in solution. This has not been systematically attempted, but there are hints that peptide formation is indeed less endothermic in the adsorbed phase than in the bulk (Bujdák and Rode 2001).

### Desorption Procedure

Direct, quantitative analysis of a mixture of AAs and peptides in the adsorbed state is not possible in the current state of characterization techniques. Their analysis is usually performed by chromatographic methods (HPLC) on solutions obtained after a desorption treatment.

The most frequent procedure for amino acid and peptide desorption is washing of the AA/oxide samples with a 0.1 M $CaCl_2$ solution. This procedure is probably inspired by clay chemistry; it is likely to displace most of the ions that are electrostatically adsorbed to the solid surface, but its efficiency is not self-obvious for amino acids held by a specific adsorption mechanism, such as a covalent bond (cf. supra). Consequently, the effective removal of organic matter from the sample should be verified after this treatment. This has sometimes been checked by IR of the remaining solid (Bujdák and Rode 1999a) and could also be done by TGA, but these techniques are not extremely sensitive and the suspicion can still be legitimately held that some minority species are not quantitatively desorbed and may even escape analysis. Indeed, in their later work, Bujdák and Rode have found that distilled water is more efficient than $CaCl_2$ solutions to remove oligopeptides from alumina, although neither treatment is quantitative (Bujdák and Rode 2003a).

The same remark holds for the original desorption procedure of Lahav et al. (1978), using 1 M $NH_4Cl$ solution.

Chloroform extraction has been used by Basiuk and Gromovoy (1993b). In opposition to $CaCl_2$ desorption, this would be expected to remove neutral adsorbed species more efficiently than ionic species.

## Amino Acid Adsorption Mechanisms

Characterizing the mechanisms of adsorption of amino acids is not a waste of time because it allows general predictions to be made, for instance on the selectivity of adsorption from a mixture of different molecules. The vocabulary referring to adsorption mechanisms is not standardized so far; the three-way classification used here is designed to distinguish between mechanisms that are *non-specific* (i.e., which can only discriminate between chemically different amino acids on the basis of their global electric charge—"Electrostatic Adsorption"), and mechanisms that are specific, i.e., they are based on the formation of a well-defined local chemical bond, either covalent or supramolecular ("Specific Adsorption by Covalent Bond Formation" and "Specific Adsorption by Hydrogen Bonding," respectively).

The possibilities for different interactions will of course depend on the acid-base properties of the amino acid. Furthermore, when amino acids are adsorbed in their globally neutral form, they may exist either as uncharged molecules ($H_2N–CHR–COOH$) or as zwitterions ($^{+}H_3N–CHR–COO^{-}$). To summarize available data, the neutral form predominates for adsorption from the gas phase on dried surfaces, and the zwitterion for adsorption from aqueous solutions, but later variations of water activity (by drying or rewetting) may change one form into the other.

## Electrostatic Adsorption

First, charged amino acids can be retained in the vicinity of a mineral surface bearing the opposite charge by simple electrostatic attraction. This situation can be envisaged for most oxide and silicate minerals. One has to distinguish minerals bearing a substitutional lattice charge (e.g. zeolites and clays: negative charge, or layered double hydroxides [LDHs]: positive charge), which is in principle constant and independent of the conditions in solution, from minerals where the surface charge originates in protonation/deprotonation of surface amphoteric groups (most often of the S–OH type, where S is a surface atom): in the latter case, the sign of the surface charge is pH-dependent, being positive at low pH and negative at high pHs.

Accumulation of compensating ions in the region of the solution neighboring a charged surface is a well-known phenomenon described in the frame of double-layer theory. Without going into the details, it is easy to understand that since the speciation of amino acids is also pH-dependent, the net sign of the electrostatic interaction between surface and amino acids may be attractive or repulsive, depending on the conditions in solution, as illustrated in Fig. 2. The predominance domains shown in the figure allow to predict the sign of the electrostatic interaction according to the particular amino acid/mineral surface couple under consideration. For instance, if electrostatic interaction was the sole factor at play, at neutral pH aspartate should be preferentially adsorbed over lysine on alumina, whose surface is positively charged, but the reverse should be true on zeolite and on silica; similar electrostatic selectivities have been recently documented by Churchill et al. (2004)

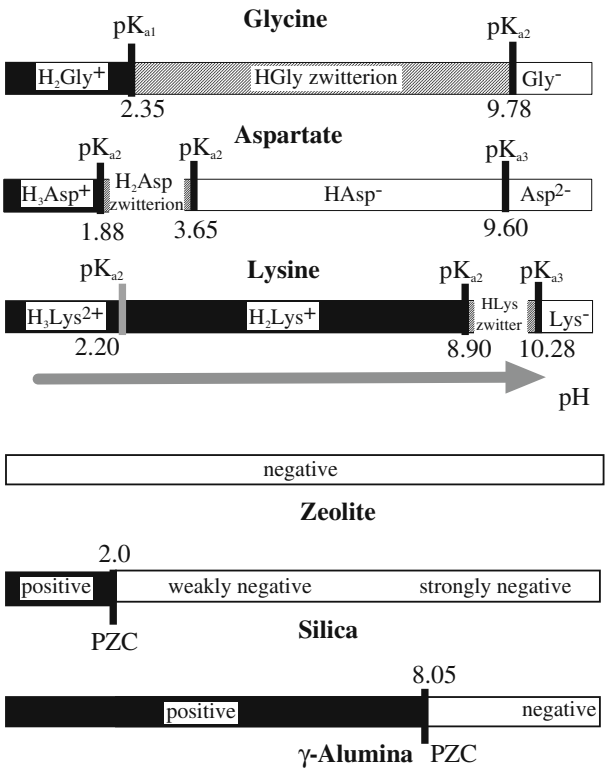



**Fig. 2** A comparison of the acid-basic speciation of several amino acids and of several oxide surfaces. *Black* positively charged, *hatched* globally neutral, *white* negatively charged

on quartz and calcite single crystals. Also, for the majority of amino acids (those having neither an acidic nor a basic side group), simple electrostatic considerations are insufficient to predict adsorption selectivities because at "reasonable" pH values, the amino acid is mostly zwitterionic, i.e., it bears zero overall charge.

Electrostatic bonding has been an important feature of Wächtershäuser (1988) model of protometabolism. He underlines the fact that many key metabolites are anions, and thus can be electrostatically adsorbed to a positively charged surface such as he assumes is the case of pyrite. In fact, this model of pyrite surfaces is oversimplified since the surface charge of pyrite can actually be negative in many circumstances (Bebie et al. 1998; Weerasooriya and Tobschall 2005; Preocanin et al. 2007).

Soon afterwards, de Duve and Miller (1991) criticized this view: "It is difficult to visualize the development, even in two dimensions, of a complex metabolic network (…) without more diverse (…) binding surfaces than those provided by a simple, charged plate." And indeed, things can be more complex than that: focusing again on the case of pyrite, one of the few experimental studies of the adsorption of amino acids and other small biological molecules indicates that negatively charged species can undergo significant adsorption on negatively charged pyrite surfaces (Bebie and Schoonen 2000), showing that a simple electrostatic adsorption model does not account for the adsorption behavior. In the same way, lysine was observed to adsorb on $TiO_2$ in small amounts at high pH (11.5), in spite of an unfavorable global electrostatic interaction since both the surface and the amino acid are negative at this pH (Roddick-Lanzilotta et al. 1998).

Because the purely electrostatic adsorption of charged molecules only depends on their net charge, it is considered as non-specific, as opposed to specific adsorption mechanisms that will be outlined in "Specific Adsorption by Covalent Bond Formation" and "Specific Adsorption by Hydrogen Bonding" and that can give rise to more discriminatory recognition of adsorbed molecules (some physicists may object to calling the latter mechanisms "non-electrostatic" since ultimately the electrostatic interaction is the source of all chemistry, but colloid chemists usually live well with this imprecision).

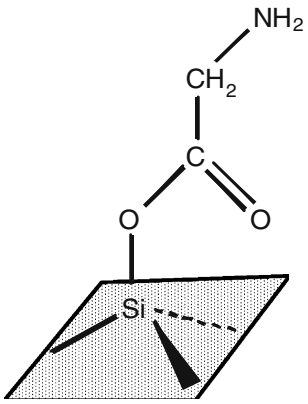
## Specific Adsorption by Covalent Bond Formation

Specific adsorption is equivalent to site adsorption and therefore each surface must have a saturation coverage for a given amino acid, depending on the number of specific adsorption sites per square $nm^2$. The nature of the specific adsorption sites has only been assessed in very special cases, on single crystal surfaces and for adsorption from the gas phase (*vide infra*).

In the older literature (Collins et al. 1988), it is taken for granted that the special reactivity of amino acids on surfaces is due to the "formation of an anhydride" with surface hydroxyl groups. Elsewhere, this postulated adsorbed form is called "surface acyl" or "surface ester." It is illustrated in Scheme 1 below for the case of glycine on silica and is obviously transferred from solution biochemistry, with a surface atom (Si here) simply replacing a carbon atom.

This altogether reasonable hypothesis was not tested until the IR work of Macklin and White (Macklin and White 1985) and Basiuk (e.g. Basyuk 1990), where bands observed at 1760 to 1780 $cm^{-1}$ were assigned to the CO stretching of the covalently bound amino acids. However, the existence of covalently bound amino acids on silica remains an open question: molecular modeling (DFT) calculations by Rimola et al. (2006a, b) indicate that the formation of this species is unfavored with a $\Delta_{formation}G°$=+25.5 to +29.7 kJ $mol^{-1}$.

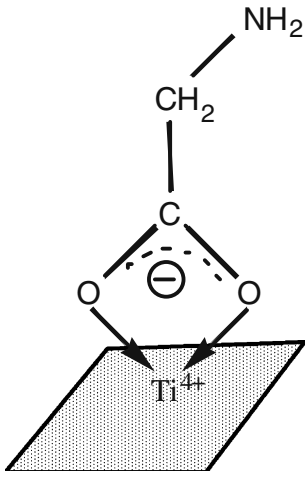
**Scheme 1** Specific adsorption of glycine on silica through covalent bond formation




These authors have suggested that the "surface anhydride" might only form by reaction with special defects consisting in strained siloxane cycles. In other words, this surface species would be produced because its formation is coupled with thermodynamically favorable siloxane ring opening. There is a neat parallel with biochemistry here, although it is not sure if it is relevant for prebiotic chemistry because silica has to be activated at high temperatures to carry strained siloxane rings: the surface ester is definitely an activated form of the amino acid, and indeed Basiuk et al. have reported that it is only formed in the absence of water, and that hydration results in rapid hydrolysis (Basiuk and Gromovoy 1993b).

On titania ($TiO_2$), on the other hand, there is little doubt that covalent binding is possible. However, special features of transition metal ion reactivity must be taken into account here. One is in fact dealing with coordination chemistry, and the localized binding models of organic chemistry cannot be transposed automatically. Thus, the best-documented example of amino acid covalently bound to a surface so far (for Gly on $TiO_2$ from the gas phase: Qiu and Barteau 2007) involves a bidentate coordinative bond to unsaturated $Ti^{4+}$ centers (Scheme 2).

**Scheme 2** Specific adsorption of glycine on titania through coordinative bond



Those unsaturated $Ti^{4+}$ centers constitute specific adsorption sites; since it is observed that only one half of them can adsorb glycine, the surface sites density is one per two unit cells or 2.65 molecules per $nm^2$, or 4.4 μmol per $m^2$ of exposed surface. This may be the only instance where surface coverage has been rationalized by the identification of specific adsorption sites.

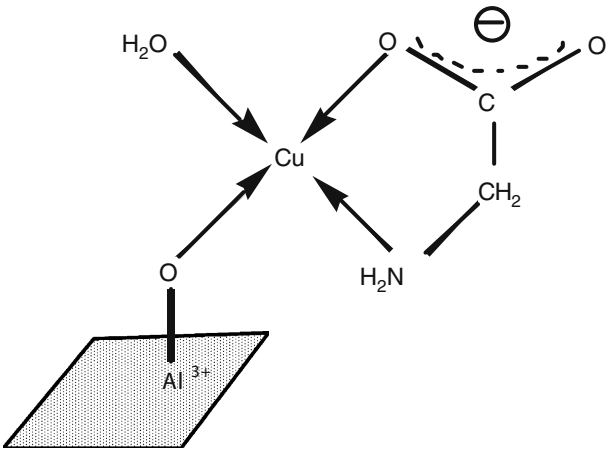
This example relates to adsorption from the gas phase on a surface previously activated by outgassing. However, the possibility of coordinative carboxylate binding in the case of adsorption from an aqueous solution onto $TiO_2$ is also demonstrated by the work of Roddick-Lanzilotta in the case of glutamate and aspartate (Roddick-Lanzilotta and McQuillan 2000), and polylysine (Roddick-Lanzilotta and McQuillan 1999), where the evidence was primarily based on *in situ* vibrational spectroscopy (ATR mode). In addition, purely macroscopic modeling of the adsorption data independently confirms this type of binding at the solution/$TiO_2$ interface in the case of aspartate (Giacomelli et al. 1995).

Conversely, it should be noted that earlier work by Fleming and Idriss (2004) on adsorption on a different face of $TiO_2$, and a different AA (proline) suggested a different adsorption mechanism: therefore, one should be warned against overgeneralization.

On $Al_2O_3$ films, Tzvetkov et al. (2004) proposed a model for glycine adsorbed from the gas phase at 300 K that was very similar to the one of Qiu and Barteau (2007) above, with "the glycinate species standing proud on the surface," this time anchored to $Al^{3+}$ rather than $Ti^{4+}$. This model was arrived at from a combination of local information (XPS, UPS, EXAFS) rather than based on adsorbate periodicity. Coordinative adsorption was probably activated since the surface complex did not form when glycine was adsorbed at 110 K, which is indeed expected for coordinative bonding.

More complicated mechanisms may also be at work in a complex medium containing e.g. metal ions in addition to amino acids. In an early paper, on the basis of EPR spectroscopy, McBride (1985) has proposed the formation of a ternary complex between glycine, $Cu^{2+}$, and Al oxyhydroxide surfaces (Scheme 3).

In this instance, $Cu^{2+}$ could be considered as a mediator of the interaction between the amino acid and the surface. A more recent example is the ternary $Cu^{2+}$/His/Y zeolite complex observed by Mesu et al. (2006).




**Scheme 3** Specific adsorption of glycine on Al oxyhydroxides through the formation of a ternary coordination complex

In the same way, Vlasova (2005) rationalized the macroscopic adsorption data of several amino acids (X) on silica in the presence of $Cu^{2+}$ through the formation of ternary complexes with formula "Si–O–CuX" with copper making coordinative bonds to both the surface silanolate and the anionic amino acid. Again, macroscopic information could lead to the same model of specific interaction in this instance as spectroscopic information did in the previous one.

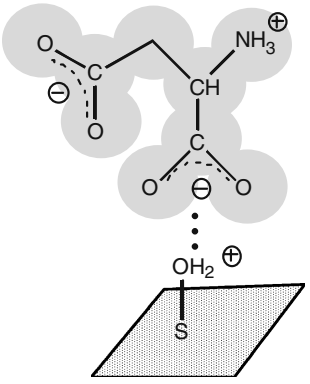
When adsorbed in the interlayer of a Cd-montmorillonite clay, glycine partly complexed the $Cd^{2+}$ ions as shown by $^{13}C$ and $^{111}Cd$ NMR (Di Leo 2000); histidine and lysine complexed the $Cu^{2+}$ ions in a Cu-saponite (Fu et al. 1996) or a Cu-montmorillonite (Szilagyi et al. 2005).

## Specific Adsorption by Hydrogen Bonding

Hydrogen bonds are weak but in cooperation they may form adducts that are both solidly held and highly specific. There are of course many examples of this in biochemistry, but such adducts can also be envisaged between a surface and an adsorbed molecule. They are usually called "complexes" in colloid chemistry, a term that may be confusing, unless one insists that they are "outer-sphere complexes." In the parlance of triple-layer theory, they reside in the "Stern layer." The adsorption is probably not activated in such cases, and therefore the adsorption-desorption reactions should reach equilibrium quickly.

In aspartic acid adsorption on kaolinite, Ikhsan et al. (2004) inferred two such outer-sphere complexes, $S-OH_2^+ \cdots (HAsp)^-$ (illustrated in Scheme 4) and $S-OH_2^+ \cdots (Asp)^{2-}$, depending on the pH value.

Another instance where such adducts have been evidenced is in the adsorption of basic amino acids (Arg, Lys, ornithine) on silica (Vlasova and Golovkova 2004). Modeling of the macroscopic data indicated a good fit with the formation of $Si–O^-\ldots(H_2X)^+$, where X is the deprotonated form of the amino acid. These two examples suggest that adducts can be formed both with protonated and deprotonated surface groups. Considering the situation from the point of view of the amino acid speciation, one can note that surface adducts may involve their cationic forms, or their anionic forms. In fact they may also involve their zwitterionic forms: Ser adsorbs on hydroxyapatite (HAP) through the formation of an "ion pair" between the positive ammonium group and negatively charged sites on the surface (Spanos et al. 2001). This ion pair was rationalized in terms of




**Scheme 4** Specific adsorption of aspartate on kaolin through the formation of a hydrogen-bonded adduct, or outer-sphere complex. S is probably Al; the precise H-bonding structure is unknown

localized electrostatic interactions but in view of the groups involved it probably has some H-bonding character.

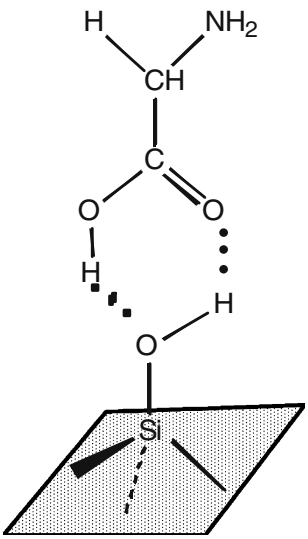
Here, one word should be said about the rather ill-defined term of "ion-exchange" adsorption. On materials such as clays or zeolites, this refers to the substitution of one charge-compensating ion by another, e.g. $K^+$ by $Na^+$, or $Na^+$ by $H_2Arg^+$ (Krohn and Tsapatsis 2006): both before and after exchange, the ion is held by electrostatic adsorption. However, on amphoteric oxides, the same term is used to characterize an adsorption mechanism where an ion causes the deprotonation of a surface S-OH group (e.g. a silanol, Si–OH) and then remains bound to the ionized surface group (in this case a silanolate, Si–$O^-$). For instance, for lysine adsorption on mesoporous silica (O'Connor et al. 2006):

$$\mathrm{Si-OH_{surf}} + \mathrm{H_2Lys^+_{solution}} = \mathrm{Si-O\cdots H_2Lys_{surf}} + \mathrm{H^+_{solution}}$$

Since the adsorbed amino acid modifies the chemical properties of the surface group, it must be specifically adsorbed, probably by H-bonding; the term of ion exchange is confusing in this case and its use should not be encouraged.

In all cases quoted above, the colloid chemistry approach only allows to write the stoichiometry of the surface adduct, not its precise structure. Recent studies combining molecular modeling and spectroscopic data independently confirmed that stable H-bonded adducts are indeed probably present on silica. When glycine was adsorbed from the gas phase, in the absence of water molecules, cooperative H-bonding between the COOH of a neutral glycine molecule and a silanol from the surface (Scheme 5) was the most stable structure (Lomenech et al. 2005; Rimola et al. 2006b).

The presence of water on the surface together with glycine changed the preferred adsorption structures (Costa et al. 2007), isomerizing the adsorbed glycine to its zwitterionic form, but here again some specific H-bonding patterns were stabilized, as also in the work of Rimola et al. (2006a) Note that whatever the actual H-bonding pattern, it




**Scheme 5** Specific adsorption of glycine on silica through the formation of a hydrogen-bonded adduct (outer-sphere complex)

must be quite well-defined and specific because glycine adsorbed on silica shows sharp spectroscopic signatures both in IR and $^{13}C$ NMR (Stievano et al. 2007).

Another molecular modeling study of lysine adsorption on quartz found that the amino acid interacted with surface groups through a combination of electrostatic interaction and H-bonding (Gambino et al. 2004, 2006); a hypothetical surface where all silanols had been replaced by methyl groups did not show any adsorption.

### Other Contributions to Amino Acid Adsorption; Towards Molecular Recognition

Specific effects different from coordinative bonding and hydrogen bonding may be invoked in principle, but there is not much conclusive evidence so far. It has been proposed that hydrophobic effects (ultimately explainable in terms of van der Waals interactions) *between adsorbed species* play a role in phenylalanine adsorption in zeolites (Munsch et al. 2001). Hydrophobic interactions *between the adsorbed molecules and the surface* have been invoked in the case of leucine oligopeptides on quartz crystals (Hitz and Luisi 2002). Since zeolites are microporous, steric exclusion effects dependent on the size of the amino acids or peptides may also be present here, but the evidence is still limited (Wijntje et al. 2006).

Note that several adsorption mechanisms may be superimposed for the same amino acid on the same oxide. On zeolite beta and faujasites, Phe was both electrostatically adsorbed as $HPhe^+$ and specifically adsorbed as the zwitterion (Krohn and Tsapatsis 2005, 2006). On silica, Basyuk reported that hydrogen-bonded and covalently bonded amino acids were formed together when adsorbed from the gas phase (Basyuk 1990).

Note also that even a single amino acid molecule could very well establish several different interactions with the surface in a phenomenon reminiscent of interactional complementarity (for a more general discussion of interactional complementarity and molecular recognition in adsorption, see Boujday et al. 2003). While the experimental evidence is still scant, molecular modeling suggests that glycine adsorbed on silico-aluminas can interact at the same time by coordinative bonding of its –COOH group to an $Al^{3+}$ center and formation of two H-bonds with surface hydroxyls (one as an H-donor and one as an H-acceptor: Rimola et al. 2007); as regards glycine adsorbed on S-defective pyrite ([100] surface), it would deprotonate to a glycinate that then forms two coordinative bonds to an exposed Lewis acidic Fe center, through both ends at the same time (Nair et al. 2007).

The possibility of interactional complementarity between mineral surfaces and small biological molecules is strengthened by the observation that randomly folded alternating Glu–Leu peptides show the formation of secondary structures such as β-sheets when interacting with some mineral surfaces (cadmium sulfide: Brack and Bertrand 1997; Bertrand and Brack 2000).

Finally, it has been recently shown that the adsorption of cysteine between the layers of a bentonite clay is coupled with a redox reaction in which $Fe^{3+}$ is reduced to $Fe^{2+}$ (Benetoli et al. 2007), and presumably cysteine oxidized to cystine in the process.

## Adsorption Selectivities

The preceding paragraph on adsorption mechanisms shows that (1) specific adsorption mechanisms are likely operating in many cases, and (2) even for electrostatic adsorption, the different speciations of different amino acids should induce clear preferences in some cases: therefore significant adsorption selectivities should be expected for mixtures of amino acids. However, experimental tests of this prediction are rare so far.

Early data by Jaffe (quoted in Ponnamperuma et al. 1982) indicate that "adsorption is dependent on the isoelectric point" of the amino acid, which is not surprising if the adsorption mechanism is electrostatic (cf "Electrostatic Adsorption" above). Friebele (1980) tried to evaluate if biological amino acids could have been selected from a mixture also containing their non-biological counterparts by adsorption on montmorillonite clays but came up with a negative answer.

The few recent data are from chromatography and separation science. Titus et al. (2003) reported that the zeolite ZSM5 has a very high selectivity for Phe and Tyr over Ala and Trp, the latter compounds being adsorbed in undetectably low amounts. No explanation was offered; the exclusion of Trp could be due to steric factors, but not that of Ala. On zeolites X, Y and β, Arg adsorption was strongly favored in (Phe+Arg) mixtures (Krohn and Tsapatsis 2006) at high pH, which is probably related with the acid-basic speciation of Arg.

Recently, Stievano et al. (2007) reported a strong selectivity for lysine adsorption in (Lys+Gly) mixtures on silica, which was also probably due to electrostatic factors, since in the conditions studied lysine was positively charged and the silica surface was negative.

Note that if the mixtures were behaving ideally, the question of adsorption selectivity would boil down to comparing the adsorption constants of the different amino acids present in the mixture. However, it seems quite likely that adsorbed amino acids can interact with each other, giving rise to non-ideality: then the adsorption behavior of given amino acids would depend on what other amino acids are present in the system, possibly giving rise to stronger selectivity.

The possible meaning of adsorption selectivity for the selection of amino acids used in protein building has been underlined in the work of Zaia et al. (e.g. Zaia 2004). They observed that the relative abundances of the various amino acid categories observe in the modern proteome do not match the tendencies for relative adsorption on clay minerals (Benetoli et al. 2007); in particular, amino acids with charged groups are adsorbed in higher amounts than those with neutral side chains, while the latter predominate in proteins. In view of the different possible adsorption mechanisms summarized in "Amino Acid Adsorption Mechanisms," it seems likely that different relative trends could be observed on different adsorbents, but this type of reasoning still is of great interest in discriminating which are the "prebiotically interesting" adsorbents.

To most researchers on the origin of life, the question of amino acid adsorption selectivity immediately calls to mind the selectivity between L- and D-enantiomers, and therefore the issue of the origin of homochirality. Tantalizing results have been repeatedly found in the literature: for instance, montmorillonite adsorbed up to twice more of the L- than the D-enantiomer of glutamic acid, but the tendency was opposite for aspartic acid (Siffert and Naidja 1992); in contrast, natural allophanes (Hashizume et al. 2002) did not discriminate between D- and L-alanine, but showed significant preferences between the enantiomers of Ala–Ala. Even natural sediments have been reported to exhibit some enantiomeric adsorption preferences (Wedyan and Preston 2005).

A concerted research effort has been undertaken to test the possible effect of surfaces in selecting L- over D-amino acids (Hazen et al. 2007, internet site). Some surfaces are naturally chiral, and enantiomorphic surface structures such as found for calcite single crystals constitute very promising candidates for the study of adsorption-induced homochirality: some calcite faces show a slight preference for the adsorption of L over D-aspartic acid, while the opposite trend is observed on other faces (Hazen et al. 2001). Other surfaces are not chiral by themselves, but in some cases there might be a theoretical basis for the energetic non-equivalence of the interaction with L- and D-amino acids: this is the case for the formation of L-Ala and D-Ala dipeptide intercalates in the interlayer region of clay minerals, as shown by Yu et al. (2001).

Oxide surfaces could also have played a role at a later stage, namely through the amplification of enantiomeric excesses in amino acids polymerization (Hitz and Luisi 2002, 2003).

A complete assessment of this issue is beyond the scope of the present paper and would no doubt deserve a full review on its own.

## Peptide Formation upon Thermal Activation

### General Findings

As mentioned earlier, there are hardly any data on eventual peptide bond formation at room temperature. On the other hand, its occurrence after thermal activation has been amply demonstrated.

For instance, with glycine, oligomers up to $(Gly)_6$ are formed on the application of wetting and drying cycles (Bujdák and Rode 1996, 1997a). Starting with preformed oligomers even allows the formation of obtain longer chains, e.g. up to $(Gly)_{11}$ from $(Gly)_5$ on alumina. Many more instances of polypeptide formation from monomers, or of oligopeptide chain elongation, can be found in the works of Bujdák, Rode et al. and other teams (see Table 4). The lengths of the polypeptide chains do not seem to go much beyond the decamer, although it is unclear if this represents a limitation of the reactivity or of our analytical techniques (cf. "Some Questions of Practical Experiment Design"). When activated forms of the amino acids were used as monomers, much longer polymers could be obtained (up to 4,000 Da molecular weight in Yanagawa et al. 1990), that even showed catalytic activity in some cases (Ito et al. 1990), but as underlined in "Polymerization During Adsorption" this is a quite different situation which eschews the thermodynamical part of the problem.

When several oxide materials were compared in similar conditions, alumina was reported to be most efficient as compared to either silica or clay minerals (Bujdák and Rode 1997b, 1999a). This means that the yields of polypeptide formation observed after a given number of WD cycles is higher on alumina than on silica, and lowest on clays. What is measured here is probably a kinetic rather than a thermodynamic effect.

Simple heating under vacuum or under inert gas generally yields the cyclic anhydrides (or diketopiperazines, DKP—Basiuk and Gromovoy 1993b; Meng et al. 2004; Scheme 6).

They are often considered as a dead end for peptide formation, and the reaction has even been promoted as a way to selectively synthesize substituted diketopiperazines (Basiuk et al. 1991, 1992; Basiuk and Gromovoy 1993c).

However, it seems that DKP can react with left-over monomers to form linear trimers (Bujdák and Rode 1997b, 2003b). It is already clear from reaction stoichiometries that the ratio of cyclic dipeptide to linear oligopeptide formation will depend on the activity of water, and indeed comparison of different procedures for WD cycles has shown that intermittent exposure to conditions of higher water activity resulted in higher amounts of linear peptides relative to DKPs (Bujdák and Rode 1997b), but the details of the reaction network need to be worked out. Once DKP is formed, the formation of trimers following the reaction:

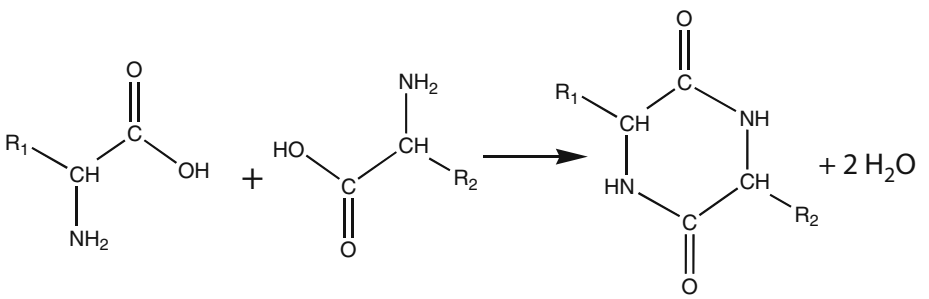
$$\mathrm{DKP} + \mathrm{X} = \mathrm{X} - \mathrm{Gly} - \mathrm{Gly}$$

apparently can occur to a large extent in an aqueous solution (Nagayama et al. 1990). This is not surprising since the formation of the product does not necessitate a net increase in the number of amide bonds.

**Table 4** Experimental studies mainly concerned with thermal activation and thermal reactivity of oxide-adsorbed amino acids

| Oxide mineral | Amino acid | Reference |
|---|---|---|
| $SiO_2$, $Al_2O_3$ | Gly, $(Gly)_2$ | Bujdák and Rode 1997a |
| Various $Al_2O_3$ | Ala, Gly | Bujdák and Rode 2001 |
| $Al_2O_3$ | (Gly–Gly), $(Gly)_3$, $(Gly)_4$, $(Gly)_5$, $((Gly)_2$+Ala), $((Gly)_2$+Leu), $((Gly)_2$+Val), $((Gly)_2$+Pro) $((Ala)_2$+Gly) | Bujdák and Rode 2003a |
| $Al_2O_3$ | Ala, Gly, Leu, Pro, Val, $(Gly)_2$, $(Ala)_2$, $(Gly)_3$, $(Gly)_4$, $(Gly)_5$ | Bujdák and Rode 2003b |
| Kaolinite, montmorillonite | pyroGlutamic acid | White et al. 1984 |
| Kaolinite, bentonite | Gly | Lahav et al. 1978 |
| Na-, Zn-, Cu- and Ni-bentonite | Ala, Gly | Lawless and Levi 1979 |
| Ca- and Cu-montmorillonite | Gly | Bujdák et al. 1994 |
| Montmorillonite, ≠ compensating cations | Gly, $(Gly)_2$ | Bujdák et al. 1996b |
| Reduced charge montmorillonite | Gly, Gly–Gly, DKP, (Gly+Gly–Ala), (Gly+Ala–Gly) | Bujdák et al. 1996a |
| Various smectites with ≠ substitutions | Gly, $(Gly)_2$ | Bujdák and Rode 1996 |
| Pyrophyllite, talc, various smectites, vermiculite, chlorite, sepiolite, attapulgite | Gly, $(Gly)_2$ | Bujdák and Rode 1999b |
| Montmorillonite, hectorite, $SiO_2$, $Al_2O_3$ | Ala (Ala+Gly) (Ala+$(Gly)_2$) (Ala+DKP) | Bujdák and Rode 1997b |
| Hectorite, $SiO_2$, $Al_2O_3$ | Gly, Ala, Pro, Val, Leu (Ala+Gly), (Ala+$(Gly)_2$) (Pro+Gly) (Pro+$(Gly)_2$) (Val+Gly) (Val+$(Gly)_2$) (Leu+Gly) (Leu+$(Gly)_2$) (Ala+Pro), (Ala+Val) | Bujdák and Rode 1997b |
| Montmorillonite, $Cu^{2+}$-exchanged hectorite | Gly, Tyr, (Gly+Tyr) | Porter et al. 2001 |
| LDH | Asp | Yuan et al. 2004 |

(Zamaraev et al. 1997) have shown that the presence of zeolite β in hydrothermal conditions accelerates the hydrolysis of DKP to linear Gly–Gly, which they considered as the starting material for further polymerization, but their data are unclear as regards the thermodynamics of polymerization. Mixed scenarios may also be considered, e.g. where DKP formation occurs by SIPF, and chain lengthening by reaction on clay minerals (Rode et al. 1997); the discussion of the many possibilities would take us too far.




**Scheme 6** Formation of the cyclic dimer (substituted DKP) from two amino acid monomers

Regarding what happens upon heating of previously dried amino acid/oxide mineral systems at higher temperatures, one sees that oxidative decomposition of the adsorbed organic material takes place starting around 200°C (Meng et al. 2004). These reactions are outside the scope of this paper; suffice it to say that the peptide bond formation step is generally well-separated from further decomposition, which is fortunate if one wants peptides to be stably formed in a range of experimental conditions that is not too restricted. However, there are some exceptions, as for instance glutamic and aspartic acid can be deaminated even at room temperature when adsorbed on montmorillonite (Siffert and Naidja 1992).

## Kinetics and Mechanism of Peptide Bond Formation

Although no formal studies of the reaction kinetics have been undertaken, Bujdák and Rode (2001, 2002, 2003b) have considered the temporal evolution of oligopeptides formed on $Al_2O_3$ maintained isothermally at 80°C to 90°C in an oven. From their data, it was obvious that dipeptide yields were still increasing at the end of the study (i.e., after 12 to 28 days of reaction) for all systems tested: a polymerization equilibrium was not yet reached (although the degree of polymerization reached 15% transformation in some cases).

At higher temperatures of course the kinetics of peptide bond formation is much faster. On silica, TGA clearly shows that cyclodimerization occurs in a matter of minutes at 150–160°C (Meng et al. 2004; Stievano et al. 2007).

It has been mentioned before that the early "surface ester" model for adsorbed amino acids was based on an analogy with organic chemistry, an analogy which suggests a mechanism for polymerization activation.

Speculative mechanisms are proposed e.g. in Basiuk and Gromovoy (1993b) and Bujdák and Rode (1997b, 1999a). It is often assumed that amino acid bonding to the surface through its –COOH or $COO^-$ moiety decreases the electron density on the carboxylic carbon and thus makes it more prone to nucleophilic attack by the $–NH_2$ group of another adsorbed amino acid. This might happen both in the case of covalent bonding (where the surface Si, Al or Ti center acts as a Lewis acid) and H-bonding (which can be viewed as an incomplete $H^+$ transfer, with the surface generally playing the role of a Brönsted acid).

Intuitive reasoning can be misleading of course, and had better be confirmed either by experiment or simulations. Recently, progress in molecular modeling has made it possible to examine reaction mechanisms by *ab inito* methods, a task that has been undertaken by Ugliengo and coworkers. They have found that the best candidates to catalyze peptide bond formation are special surface sites composed of one Brönsted acidic center neighboring a Lewis acidic center (Rimola et al. 2005), an arrangement likely to be found on aluminosilicates such as feldspar (Rimola et al. 2007). The adsorption of amino acid analogs to such sites lowers the activation barrier for amide bond formation from 209 kJ $mol^{-1}$ in the gas phase to 67 kJ $mol^{-1}$ (Rimola et al. 2007), i.e., by 68%, while on a silica surface (which lacks Lewis acidic centers), the decrease in the activation barrier is only 10% (Rimola et al. 2006b); note however that the presence of water as a proton transfer adjuvant causes a further 13% decrease.

These figures were obtained for glycine adsorbed as an uncharged (non-zwitterionic) molecule, when the role of the Lewis acidic center (a coordinatively unsaturated $Al^{3+}$ ion) was mainly to anchor the amino acid on the surface through the $–NH_2$ end, while the Brönsted acidic center activated the –COOH moiety as said above. Thus, chemical intuition is mostly confirmed, but considerably enriched because a rigorous treatment allows to account for such effects as geometric strain and dispersion interactions.

Similar studies on adsorbed zwitterionic and anionic amino acids would be enlightening.

### Peptide Formation Reaction Selectivity

Since it is firmly established that adsorption followed by drying can efficiently induce the formation of amide bonds between amino acids, the next step is to determine if "meaningful" peptide sequences could be selectively formed in this way. Indeed, there are many observations of polymerization selectivity in the literature, especially in the work of Bujdák and Rode.

For instance, on silica and alumina, the (Ala+Gly) reaction preferentially forms Ala–Gly over Gly–Ala. The preference is not very high, since the Ala–Gly/Gly–Ala ratio is <2 in most cases. There is also a slight excess of Gly–Gly–Ala over Ala–Gly–Gly (Bujdák and Rode 1997b). Proline behaves in the same way as alanine, but other hydrophobic amino acids (Leu, Val) show the opposite trend, i.e., the Gly–X dimer is formed preferentially to the X–Gly dimer (Bujdák and Rode 2002). These trends were explained in terms of classical organic chemistry (e.g. inductive effects) and were not considered to be surface-specific (indeed the same trends were observed in the surface-independent SIPF mechanism).

In (Gly+Tyr)/clay systems Porter et al. have reported non-random synthesis of certain (Gly, Tyr) oligomer sequences (Porter et al. 2001). Also noteworthy was the fact that with respect to monomolecular Gly/clay or Tyr/clay systems, the distribution of oligomers is significantly perturbed by the presence of the second amino acid; for instance, in Gly/clay the yield of oligomer formation quite logically decreased between $(Gly)_2$ and $(Gly)_6$; when an equal amount of Tyr was added, $(Gly)_2$ was specifically depleted.

Much more selectivity data may be found in the works quoted in Table 4, but it is still difficult to discern general tendencies, and even more so to attempt a general explanation. Nevertheless, the observation of significant surface polymerization selectivity is encouraging from the point of view of prebiotic chemistry.

## General Discussion and Directions for Future Work

In 1991, de Duve and Miller (1991) wrote that "If things are different on surfaces, then this should be demonstrated experimentally." At the present time, it can be said with confidence that things are indeed different on surfaces, and in a way that induces cautious optimism for surface polymerization scenarios, but we are still very far from a general understanding of exactly how different they are.

The preceding paragraphs hopefully gave an idea of the scientific advances on various aspects of the problem of surface polymerization.

It is definitely a fact that amino acid polymerization is favored by adsorption, at least if the latter is followed by drying at moderately high temperatures. It remains unclear if adsorption without drying could result in significant polymerization: this would require quite simple ageing experiments, which unfortunately are too lengthy, and too dull, for most funding agencies.

We are starting to understand at the molecular level the various possible mechanisms of amino acid adsorption on oxide surfaces. As it turns out, the situation is rather complicated and many different mechanisms may come into play according to the specific surface, the specific amino acid, and the experimental conditions (pH, ion strength, etc.) under consideration. This conclusion may seem discouraging at first, but to look at the bright side it means that the surface chemistry of amino acids is richer and therefore more interesting than previously expected. Also, the burden of unraveling this chemistry is not left to

prebiotic chemists. Many others are quickly contributing to our understanding of this field, with relevant results from fundamental surface chemistry to biocompatibility that can help design better prebiotic experiments.

Adsorption selectivities from amino acids mixtures should probably be studied more systematically (cf. "Adsorption Selectivities"). When devising such experiments, one is faced with the choice between a huge number of possible systems. Brack et al. have suggested to concentrate on simple amino acids mixtures whose ordered polymers might show remarkable properties such as special folding patterns, offering the (Glu+Leu) or (Asp+Leu) couples as an example (Brack and Bertrand 1997; Bertrand and Brack 2000). Of course, after studying the adsorption selectivities in such systems, one should also study the selectivities of thermal polymerization, and especially the possibility of forming regularly alternating polymers. Whatever little is know about polymerization mechanisms in the adsorbed state does not allow one to predict what factors will govern polymerization selectivity, but practical polymerization experiments should be carried out in a close dialogue with characterization of adsorption mechanisms, and molecular modeling.

The problem of choosing the right system also implies choosing the right adsorbing surface. Of course it is preferable to study minerals that may realistically have been present in the hadean period. Speculation on those has been offered by Smith et al. (Parsons et al. 1998; Smith 1998) The earliest studies concentrated on clay minerals; silica, alumina and titania have been much studied, because their surface chemistry is quite well-known and they may constitute reasonable and simpler models of naturally occurring minerals. However, very little experimental data are available on other minerals that may have played an important role, especially Fe minerals. Regarding the sulfides that have been the object of intense speculations in prebiotic chemistry, although recent molecular modeling studies have been carried out, there have been no experimental tests of their efficiency for amino acid polymerization.

Finally, a later step could involve the study of activation mechanisms different from simple heating, such as peptide formation under irradiation (Onoe et al. 1985).

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