Synthesis in prebiotic clay environments induced by radiation

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Abstract: In this paper we exemplify a biased synthesis that can be relevant in primitive scenarios. We perform experiments simulating a possible prebiotic environment, in which an organic compound is adsorbed in soil and exposed to an energy source. To this end, carboxylic acids were adsorbed in a clay mineral and the systems were exposed to radiation. We observed that radiation decomposition in solution changes drastically if the system contains a clay mineral. Both solid surfaces and radiation play an important role.

Introduction

Despite the importance of individual gas and solution phase reactions in prebiotic monomer synthesis, it is difficult to envision the synthesis of complex macromolecules and their assembly into complex systems in the absence of a multiphase system. The contribution of a solid phase is of great relevance to the experimental simulation of the prebiotic Earth (Lahav & Chang 1976, 1982; Negrón-Mendoza *et al.* 1996; Ramos-Bernal & Negrón-Mendoza 1998; Lahav 1999). The most geologically relevant solid surfaces to promote chemical reactions on the primitive Earth are clays.

If we assume chemical reactions occur completely randomly, then we should expect to form: (a) several by-products; (b) structural isomers; and (c) optical isomers. All of these products clearly decrease the yield in a given synthesis. In order to synthesize a specific compound without such drawbacks, it would be necessary to have biased pathways in a reaction as an indispensable condition for the reproduction – or near reproduction – of a given set of molecules. Such biased character would narrow the products of the reaction and facilitate the accumulation of end products. The question is what conditions can restrict the synthetic pathways? A possible way may be through the use of solid surfaces, because they have several roles: (1) they achieve the adsorption of monomers that give rise to highly concentrated systems; (2) they facilitate condensation and polymerization reactions; and (3) they have a surface that may serve as a template for specific adsorption and synthesis of organic molecules.

To induce chemical reactions on these surfaces it is important to consider an energy source. In multiphase systems this source needs to be available, abundant and efficient to promote chemical reactions. Natural energy sources such as radioactive decay, cavitation and triboelectric energy

(i.e. energy of mechanical stress) may have a great importance in those multiphase scenarios, because they are also penetrating sources of energy (Negrón-Mendoza *et al.* 1996).

In this paper, our interest lies in: (1) experimentally showing that biased synthesis might have occurred in geologically relevant conditions on the primitive Earth; and (2) discovering whether a solid surface plays a role in the biased reaction behaviour for some organic molecules. To that end we choose a simple chemical system: a carboxylic acid adsorbed in a clay mineral and exposed to radiation. The reaction induced in this system follows a preferential chemical pathway over other possible pathways, in which both solid surfaces and radiation play important roles.

The possible role of clays in prebiotic chemistry

An important aspect in simulated experiments related to chemical evolution on Earth is their relation with a geologically relevant scenario. Clay minerals are considered important to chemical evolution processes due to their properties, ancient origin and wide distribution. Clays are ubiquitous minerals on the Earth and it is very likely that they appeared in the early steps of the formation of our planet. The analysis of the Isua sediments (in Greenland) showed that metamorphic clays may have been present at least 3.8×10^9 years ago, (Moorbath 1995). While various clays probably formed on the continents of the Earth in Archaean times, the largest area of clay production was the seabed. The genesis of continental smectites can be traced back to 3 or 4 billion years ago (Odin 1988).

Some properties and structural characteristics of clay minerals

Clay is a natural, earthy, fine-grained material that develops plasticity when mixed with a limited amount of water. This property is its most prominent macroscopic characteristic
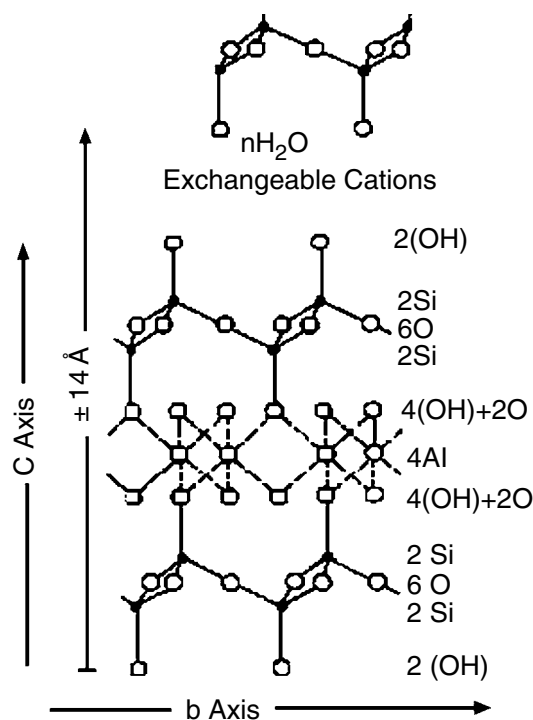
Fig. 1. Structure of montmorillonite.

and is related to its microscopic structure. The components of clays are silica, alumina, water and appreciable quantities of alkaline earth elements. The individual structural units are measured in angstroms, but their aggregates are measured in micrometers per diameter. From the crystal lattice standpoint, clays have the following structure. The individual units are formed of parallel plates stacked one above the other. Montmorillonite is a three-layered clay, where each lamina has an octahedral alumina sandwiched between two tetrahedral silica layers. The interlamellar channel is the name of the space between the silica layers (Swartzen-Allen & Matijevic 1974). The relative number of tetrahedral and octahedral sheets in the parallel plates varies from clay to clay. For example, in kaolinite its proportion is 1:1 and in montmorillonite it is 2:1. This composed unit is continuous in two directions of a plane and in the perpendicular c direction forms packets of two to 15 elementary units.

To these microstructural aspects of clay particles, we should now superimpose the electrostatic phenomena. Here the most important characteristic is the isomorphous substitution of metallic ions within the lattice. For example, Al^{3+} or Fe^{2+} can replace Si^{4+} in the tetrahedral layer and Mg^{2+}, Fe^{2+}, Zn^{2+}, Ni^{2+}, Li^+ and other ions may substitute Al^{3+} in the octahedral sheet. These substitutions create an electrical imbalance with a net negative charge on the structural units. The negative charge prevails at all pH values above 2 or 3. Counterions or interstitial cations (such as Na^+, K^+, Ca^{2+}, etc.) in the usually watery interlamellar space compensate for the negative charge.

A prominent phenomenon related to the counterions located in the interlamellar space is their exchangeability with respect to other metallic cations. The particular distinction of the montmorillonite structure from the other types is that water, free inorganic cations and polar molecules can occupy the interlamellar space. These cause the lattice to expand in the direction of stacking. X-ray diffraction methods show this expansion. The basal distance may vary from 10 Å in totally collapsed montmorillonite to 20–50 Å, depending upon the exchangeable cation (Anderson & Banin 1975). Clays can bind organic compounds by van der Waals, ion–dipole and dipole–dipole interactions. Such interactions can be expected to play an important role in chemical evolution, as first pointed out by Bernal (1951). Figure 1 shows the proposed structure of montmorillonite according to Edelman & Favejee (1940).

At neutral and acid pH ranges, the edges of the clay present a positive charge. The central atom of the octahedral layer is the origin of this charge (Nicol & Hunter 1970; Swartzen-Allen & Matijevic 1974).

Experimental procedures

Materials and glassware

The experimental part is divided into two stages: (1) radiolysis of aqueous solutions of the carboxylic acid; and (2) a study of the heterogeneous radiolysis of the water–carboxylic acid–clay system.

The carboxylic acids studied were malonic, succinic, pyruvic, acetic and aconitic acids, all of which are related to metabolic pathways. The solid surface used as a substrate to anchor the organic molecules was Na^+-montmorillonite from Crook County, WY, USA, clay mineral standard batch SWY-1. This natural rich montmorillonite, which is not homoionic, is referred to as Na^+-montmorillonite in this paper, and has structural formula $M_{0.9}^-(Si_{7.69}Al_{0.31})(Al_{3.07}Fe_{0.36}^{3+}Fe_{0.05}^{2+}Mg_{0.05}O_{20}(OH)_4)$ according to Heller-Kallai (1975). This montmorillonite has substitution within the lattice of Al for Si in the tetrahedral coordination and Mg and Fe in the octahedral sheet. The thickness of the interlamellar space is influenced by various factors, and it is strongly related to the swelling behaviour of the montmorillonite by water molecules. Generally the c-axis spacing is between 10 and 12.5 Å (Van Olphen & Fripiat 1979).

The glassware was cleaned with a sulfo-nitric solution according to the procedures recommended in radiation chemistry (O'Donnell & Sangster 1970).

Preparation of solutions

All chemicals used were of the highest purity available. The aqueous solutions of carboxylic acids were 0.1 M, at pH 3. The oxygen was removed by passing argon through the solutions.

Solutions of carboxylic acids–Na⁺-montmorillonite complex

300 g of clay were degassed during 1 h in 5 ml glass tubes adapted with a stopcock. These tubes were put in an atmosphere bag filled with argon and were mixed with 3 ml of deaerated 0.1 M solutions of the carboxylic acids. The

amount of the acid was calculated in order to remain below the cation exchange capacity of the clay. The pH in the clay samples changed from 3 to 5. Some samples of the clay–acid mixtures were adjusted to pH 3 and another set were left with pH 5. The extent of binding changed according to the proportions of acid and exchangeable cation, and was in the range 6–69% (Yariv et al. 1966; Hedges 1977). For acetic acid, the amount of binding was 40% after 22 h of equilibration. The mixtures were irradiated as described in the following section. After irradiation, the sample was centrifuged at 14 000 rpm in an Allegra 64R centrifuge, and the supernatant was removed and analysed by gas–liquid chromatography. The clay was recovered from the solutions, washed with water and finally dried at 50 °C. The clay was analysed by infrared spectroscopy (Perkin Elmer model FT-IR Paragon 500) using bromide potassium disks.

Irradiation

The irradiation was carried out in a high-intensity gamma source of ^{60}Co (Gammabeam 651 PT). The radiation doses were in the range 46–300 kGy. The dosimetry was performed by the change of ferrous ion to ferric ion due to the influence of the radiation, under a system known as ferrous sulfate–cupric sulfate dosimetry (O'Donnell & Sangster 1970). The irradiation was made at room temperature (22 °C).

Analysis of the products

Gas products were described according to the findings of Negrón-Mendoza et al. (1984). For the non-volatile products, a measured amount of the irradiated solutions (or supernatant in the case of the clay samples) was evaporated until dry. Then methyl esters were prepared following the method of Negrón-Mendoza & Ponnamperuma (1976). The analysis was carried out in a gas chromatograph Varian series 3700, using a glass column (1.82 m in length with an internal diameter of 4 mm) packed with Silar 7C. The identification of the products was made by mass spectrometry. For the gas chromatograph/mass spectrometry analysis a capillary column of methyl silicon (12 m in length with an inner diameter of 0.33 μm) was used. This chromatograph was coupled to a mass spectrometer HP model 5970.

Results

Gaseous products

Gaseous products were detected and identified in all the systems under study, and they were found to be CO_2 and H_2. A labelled experiment carried out with ^{14}C-acetic acid showed that the CO_2 was formed from the irradiated acid (Ramos-Bernal & Negrón-Mendoza 1992). The production of CO_2 was greater in samples with clay than in solution, by about one order of magnitude. Its formation increased as a function of the dose. The source of H_2 is from the radiolysis of water and from the abstraction reactions produced during the radiolysis.
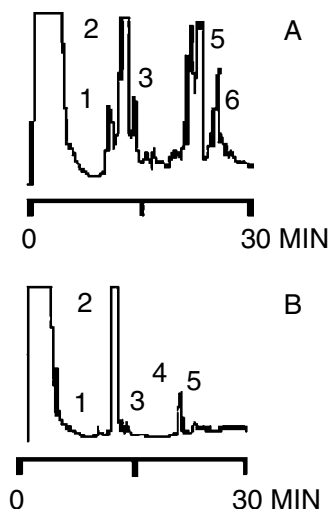

Fig. 2. Gas chromatogram of the methyl esters formed by the irradiation of malonic acid 0.1 M: (A) in the absence of clay; (B) in the presence of clay. Methyl esters of: (1) pyruvic ($CH_3(C\!\!=\!\!O)CO_2H$); (2) malonic ($HO_2C\!-\!CH_2CO_2H$); (3) succinic ($HO_2C\!-\!CH_2CH_2CO_2H$); (4) carboxysuccinic ($HO_2C\!-\!CH_2CH(CO_2H)CO_2H$); (5) di-carboxysuccinic, the dimeric product ($HO_2C\!-\!CH(CO_2H)CH(CO_2H)CO_2H$); (6) tricarballylic ($HO_2C\!-\!CH_2CH(CO_2H)CH_2CO_2H$) acids.

Samples without clay

The irradiation of aqueous carboxylic acid produced many compounds. For example, from acetic acid carboxylic acids related to the Krebs cycle were produced, such as succinic, citric, aconitic, malonic, malic and β-hydroxy-β-methyl-glutaric acids. The principal feature of these series of experiments was the production of the dimer of the acid as the main method of decomposition of the target compound. For example, in the radiolysis of acetic acid (CH_3CO_2H), the main product was succinic acid $(CH_2CO_2H)_2$, the dimeric product, which represents a conversion of 85% from the target compound. For the irradiation of succinic acid, the dimer $HO_2CCH_2\!-\!(CHCO_2H)_2\!-\!CH_2CO_2H$ was the main product. The formation of CO_2 from the decarboxylation reaction was only 7%. Moreover, the percentage decomposition of the target compound increased as the dose increased. Figure 2(A) shows a typical gas chromatogram for one of the acids under study, malonic acid. The main product was formed by a dimerization reaction. Table 1 summarizes the main results from the different acids under study. At the range considered in our study, the formation of the products was independent of the pH and the concentration of the target compounds.

Samples with clay

In the presence of clay the number of products decreased considerably. The behaviour of the samples at pH 3 was the same as that at pH 5. For example, with acetic acid, the production of the dimer was 30% and the formation of carbon dioxide increased to 71%. With succinic acid–clay radiolysis, the polycarboxylic acid formed was 5%, mainly as the

Table 1. *A comparison of the products formed from the irradiation of carboxylic acids in aqueous media with and without* Na^+-*montmorillonite*

Acid	Principal reaction without clay	Main products	Principal reaction with clay	Main products
Acetic	Dimerization	Succinic and tricarballylic acids	Decarboxylation	Methane and CO_2
Aconitic	Addition	Tricarballylic and citric acids	Decarboxylation	Itaconic acid and CO_2
Malonic	Dimerization	Dicarboxy-succinic and succinic acids	Decarboxylation	Acetic acid and CO_2
Pyruvic	Dimerization	Dimetil-tartaric acid	Decarboxylation	Acetaldehyde and CO_2
Succinic	Dimerization	Succinic dimmer	Decarboxylation	Butanoic acid and CO_2

dimeric product. Figure 2(B) shows the chromatogram of the acids formed from malonic acid irradiated in the absence and presence of Na^+-montmorillonite.

The main pathway of decomposition for clay-irradiated samples was a decarboxylation reaction, the loss of one carbon atom as CO_2. The percentage production of the dimer decreased as a linear function of the increase in dose.

Infrared and X-ray analysis

According to the X-ray data the interlamellar channel of the clay increased from 11 to 13.56 Å, indicating that the organic molecules occupied such a place after adsorption. The permanence of the organic molecules in the interlamellar space might be due to hydrogen bonds with water molecules, which are directly coordinated to polar cations (Yariv 1966), or by van der Waals interactions.

The clay–organic acid system was analysed by infrared spectroscopy. The spectra of the system under study presented several features that indicate an interaction between the organic acid and the Na^+-montmorillonite.

The infrared spectra of the Na^+-montmorillonite-acid complex showed characteristic bands of adsorbed acid. A band at 1550 cm^{-1} showed that the acid is in the ionized form (Bellamy 1989). Similar features were observed by Naidja & Siffert (1989) for the sorption of glutamic acid on different clays and by Yariv *et al.* (1966) for benzoic acid.

After irradiation other changes appeared. The Si–O out-of-plane vibration centred at 1042 cm^{-1} was broader and shifted to 1005–1010 cm^{-1}. The small band of the Al–OH–Fe^{+3} bending mode at 870 cm^{-1} decreased. These bands remained the same after clay was washed and heated for 1 h at 80 °C.
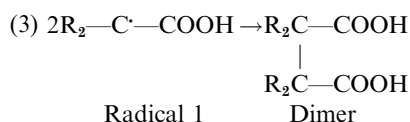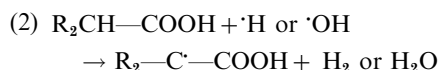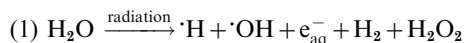
Discussion and general remarks

A more plausible and realistic way of simulating the environment that could resemble the primitive Earth would require the consideration of multiphase systems. However, most of the work done to simulate the primitive Earth has been concerned mostly with homogeneous phases, rather than heterogeneous ones. In this respect, the most geologically relevant and abundant surfaces on the primitive Earth were clays. For this reason we consider them as a good model for a multiphase system.

At the pH used in this study, the acids are probably bound to the clay mainly by van der Waals interactions. Also, carboxylic acids can enter the interlamellar space as neutral polar molecules, where they form hydrogen bonds with water molecules. Dissociated acid is also identified and this may be formed according to the following reaction:

Na^+-montmorillonite $+$ HO—CO—R $\rightarrow$
    H^+-montmorillonite $+$ Na^+—OCO—R.
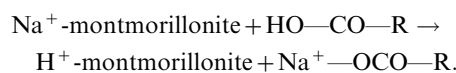
Our results show a maximum adsorption at an acidic pH, with no buffers present on natural Na^+-montmorillonite. It is important to note that such an acidic pH most probably did not existed in the primitive Earth as a whole. For this reason, the data presented in this work is pointing to the relevance of particular micro-environments in the studies of the origin of life, in which we may encounter such extreme environments which favour the adsorption of carbon compounds such as organic acids and nitrogenous bases (Perezgasga *et al.*, in press) relevant to life systems.

In an aqueous system the radiation interacts with water molecules. Very reactive species are formed due to this interaction (H, OH, e_{aq}^-, H_2 and H_2O_2). Such species attack the carboxylic acid molecules in a secondary way, mainly attacking those that are not bound to the clay (when clay is present), yielding the following observed products:

(1) $H_2O \xrightarrow{\text{radiation}} \cdot H + \cdot OH + e_{aq}^- + H_2 + H_2O_2$

(2) R_2CH—$COOH + \cdot H$ or $\cdot OH$
        $\rightarrow R_2$—$C\cdot$—$COOH + H_2$ or H_2O

(3) $2R_2$—$C\cdot$—$COOH \rightarrow R_2C$—$COOH$
                                                            |
                                                  R_2C—$COOH$
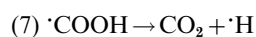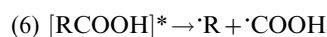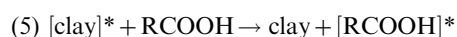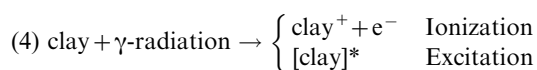   Radical 1   Dimer

In the systems without clay the main reactions induced by radiation take place via free radicals. The principal reaction is the dimerization.

In contrast, in the presence of clay, the results showed that there are changes in the mechanism. Firstly, the number of products diminished and the generation of CO_2 increased linearly with the increase in radiation dose. Thus, there is a preferential way of decomposition via the decarboxylation reaction. The main products obtained are CO_2

and the corresponding acid with one carbon atom less than the target compound. This behaviour has also been observed after prolonged heating of fatty acids with Ca-montmorillonite to various temperatures (Johns & Shimoyama 1972).

We observed two catalytic effects, one of them being produced by the clay itself. It is possible that an oxidation–reduction reaction takes place at the edges of the crystal. The acid donates an electron to the Lewis acid sites in the mineral that correspond to the charged edges or the Fe^{3+} within the clay, in a similar fashion to Kolve electrolysis (March 1968). The small band in the infrared spectra associated with Al^{3+}, Fe^{3+} or Mg^{2+} decreased indicating that an oxidation process takes place. The dissociated forms of the acids decarboxylate more easily than the non-dissociated acids (Fripiat & Cruz-Cumplido 1974).

The second catalytic effect is due to the action of ionizing radiation on the clay–organic system. In this case, the clay may play the role of an energy moderator in the following proposed pathway:

$$(4) \; clay + \gamma\text{-radiation} \rightarrow \begin{cases} clay^+ + e^- & \text{Ionization} \\ [clay]^* & \text{Excitation} \end{cases}$$

$$(5) \; [clay]^* + RCOOH \rightarrow clay + [RCOOH]^*$$

$$(6) \; [RCOOH]^* \rightarrow \dot{R} + \dot{C}OOH$$

$$(7) \; \dot{C}OOH \rightarrow CO_2 + \dot{H}$$

As was observed in previous studies (Ramos Bernal & Negrón-Mendoza 1998), the present results suggest that the clay alters the reaction mechanism in a preferential way for some reactions, acting as moderator in energy transfer processes. In the case of carboxylic acids, decarboxylation predominates when the clay is present, whereas other reactions take place when it is not.

According to the literature, the strong catalytic action of oxides and clays in heterogeneous radiolysis is connected with the formation under irradiation conditions of surface defects, namely non-equilibrium charge carriers (Garibov et al. 1982). The energy of the radiation may be partially deposited in the clay, leading to excitation and ionization. The energy taken up by the sorbent is transferred to the adsorbed substances, both water and acid molecules. Energy transfer to water molecules produces chemical decomposition to the adsorbed water molecules. In turn, this effect raises the yield of molecular hydrogen, e_{aq}, H and OH radicals (Garibov et al. 1982). On the other hand, energy transfer to the acid molecules produces radicals. These radicals can be trapped by free charge carriers (either electrons or holes) and undergo subsequent chemical transformations. The considerable increase in the radiochemical yield of CO_2 in the heterogeneous radiolysis of the carboxylic acid is evidence in favour of the assumption that these solids may transfer the adsorbed energy of the ionizing radiation to molecules adsorbed on their surface. Garibov et al. (1982) have established that the main factor responsible for the radiation–catalytic activity, i.e. the capacity of the catalyst to effectively transfer adsorbed energy, is the width of the forbidden gap.

We have shown experimentally that radiation-induced reactions in carboxylic acids are an example of preferential synthesis, as long as the acid is adsorbed on a solid surface. The radiolysis of the clay–acid system follows a definite path (oxidation) instead of going through several modes of simultaneous decomposition. This behaviour is important for prebiotic synthesis because solid surfaces can channel the energy in a different manner, so as to bias the reaction in a preferable path to produce non-random products that are formed under plausible prebiotic conditions.

Acknowledgements

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