

THERMOCHEMICAL ASPECTS OF THE CONVERSION OF THE GASEOUS SYSTEM CO₂–N₂–H₂O INTO A SOLID MIXTURE OF AMINO ACIDS

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Abstract

Conversion of the gaseous mixture CO₂(g)+N₂(g)+H₂O(g) to a solid amino acid condensate in an electric discharge plasma has high efficiency of the energy transfer from the different plasma components into chemical processes. The basic activation process is activation of the N₂ metastable electronic state, followed by formation of NCO* and ON–NCO free-radicals and generation of many reactive radicals. These radicals help to overcome the high activation energy of thermal dissociation of N₂ to N (950 kJ=9.846 eV).

The major product is a statistical polycondensate containing the amino acids: arginine, lysine, histidine, methionine, glycine, alanine, serine and aspartic acid. This information was obtained by comparing the IR spectra of the products with reference IR absorption spectra of pure components. Identification of the individual amino acids in the solid product was performed by HPLC, when samples were dissolved using 6 M HCl applied at 100°C for 24 h. Properties of the condensate were estimated using thermogravimetric analysis. Small amounts of oxamidato complexes and oligo pyrrole structures are formed on the electrode surface giving the surface catalytic properties. The gas cleaning process has practical applicability (production of useful fertilizers, reduction of the CO₂ concentration in the atmosphere) and may also contribute to explanation of the origin of life on Earth.

Keywords: amino acids, CO₂ utilisation, electric discharge, nitrogen fixation, origin of life on Earth, oxamidato complexes, tetra-pyrrole complexes

Introduction

Conversion of the gaseous system CO₂–N₂–H₂O into a solid mixture of amino acids and other products appears to be important technology for several reasons. This process may contribute to lowering of CO₂ abundance in the atmosphere. Carbon dioxide annual emissions produced by human activities in burning coal, oil, and natural gas, and by transport, amount to over 7 billion tons of carbon or almost 1% of the total CO₂ mass in the atmosphere [1]. The concentration of CO₂ in the atmosphere has increased from about 280 ppmv, before the industrial revolution, to 358 ppmv by 1994. The results of long-lasting measurements of CO₂ concentration in the atmosphere show the regular increase in concentration and the accelerating growth rate. The

IPCC [2] concluded that ‘the balance of evidence suggests a discernible human influence on the global climate’.

The natural greenhouse effect raises the temperature of the planet by 33°C, thus making it habitable. On average, 343 W/m² of sunlight fall on the earth, roughly 1/3 of which is reflected back into space. The other 2/3 reaches the ground, which re-radiates it as longer wavelength, infrared radiation. Some of it is blocked by greenhouse gases, thereby warming the atmosphere. Naturally-occurring greenhouse gases include water vapour, carbon dioxide (CO₂), methane (CH₄) and nitrous oxide (N₂O). Any factor which alters the amount of radiation received from the sun or lost to space may influence the climate. Thus, any significant enhancement of the greenhouse effect is a cause for concern. Human activity is emitting extra amounts of greenhouse gases, which will alter the amounts of radiation trapped by the atmosphere and so may have an effect on climate. Carbon dioxide emissions are responsible for over 60% of the ‘enhanced’ greenhouse effect [3].

The natural carbon cycle influences the rate at which CO₂ from human activity accumulates in the atmosphere. Carbon is exchanged over a period of years between the atmosphere, oceans, and terrestrial biosphere; over longer time-scales it is deposited as sediments and eventually, on geological time-scales, as sedimentary rocks. Carbon dioxide has a long lifetime in the atmosphere, from 50 to 200 years (depending upon which sink is involved). Human activity is responsible for almost 30% of the free CO₂ levels, which continue to increase by almost 10% every 20 years [4].

The IPCC has used emission scenarios and climate models [2] to make projections about future climate changes. There are uncertainties that remain in climate modelling, but confidence in the models has increased in recent years. The mean global surface temperature has increased by about 0.3 to 0.6°C since the late 19th century – when the instrumental record began – and by about 0.2 to 0.3°C since 1955. Using the emission scenarios, the global mean temperature will increase by 0.9 to 3.5°C by the year 2100, relative to 1990. The average rate of warming would probably be greater than any seen in the last 10 000 years.

Sea-level rise is another important consequence of climate change. The global sea-level has risen by about 10–25 cm over the last 100 years. The temperature would continue to increase even after stabilisation of the greenhouse gas concentrations in the atmosphere, because of the thermal inertia of the oceans. Increased temperatures will have caused some expansion of the sea water, and the retreat of glaciers and ice caps will also have contributed to the increase. By 2100, the sea level is projected to rise by between 13 and 94 cm due to the global melting of glaciers in Greenland and Antarctica [5].

There is also the possibility that unusual weather events, such as severe storms and hurricanes, may become more frequent. The altering in ocean circulation, such as is the Gulf Stream and El Nino, can also take place. Ecosystems, agriculture and forestry, and human health are sensitive to the climate. The range of diseases such as malaria could increase.

Some ecosystems may be unable to adapt to climate change at an adequate rate. If the rate of climate change can be limited to a low level, then natural and human sys-

tems will find it easier to adapt. The way to slow the rate of change is to reduce emissions of greenhouse gases. There are various ways of achieving this. Our work participates in developing such methods.

On the other hand, CO₂ is an important carrier of carbon, which can be used as a source for the chemical industry, especially for the technology of fertilisers, polymers, pharmaceuticals, fuels (using the oil wastes), etc.

The behaviour of chemical systems under the influence of various physical fields clearly shows the important effect of the simultaneous influence of chemical catalysts and the physical fields. All these methods show a high degree of energy conversion of the physical field into the chemical process.

One of the most important co-effects with chemical reaction was found in the application of non-thermal plasma-based methods, working with electric discharges of both polarities. This form of discharge arises at higher currents, after and together with, regular dc corona pre-discharges. The system has been successfully used in new technologies for suppressing the toxic components in exhaust gases [6–10].

The primary importance for conversion of the gaseous system CO₂-N₂-H₂O into a solid condensate of amino acids should be metastability of the intermediate gas components in comparison with the product:



while the activation energy E_a of reaction (1) can be efficiently recovered for the further chemical process. The high degree of conversion and high rate of reaction at rapid flow of the reacting gaseous mixture make process (1) interesting for practical use. Since process (1) represents a significant production of amino acids in which the activation energy is largely recovered, it can be accepted as an autotrophic process responsible for the early evolution of life.

The precursors important for formation of RNA and DNA bases can be produced by an atmosphere containing, in addition to CO₂-N₂-H₂O, also hydrocarbons with or without double-bonded carbon atoms and cyclic molecules (like benzene and its derivatives) [8]. The source of these compounds could be volcanic activity and hydrolysis of metallic carbides. The atmosphere is then enriched by new radicals (NCO* remains a stable constituent), polymeric fragments, transition metal complexes, pyro- and polyphosphates or polymers with metallic conductivity (polypyrrole). From this chemical base could grow the DNA and RNA nucleotides and enzymes in their present form. Although the conversion process of the system CO₂-N₂-H₂O-CH_x is much more complicated, it can be treated theoretically and can also be applied in practical life for exhaust gas cleaning and recycling of the hydrocarbons produced in the crude-oil processing industry, as described [11]. Some starting information will be presented.

Experimental

A high-voltage, spontaneously pulsing, direct current electric discharge system operating in corona discharge geometry (details given in [11]) was used for experiments.

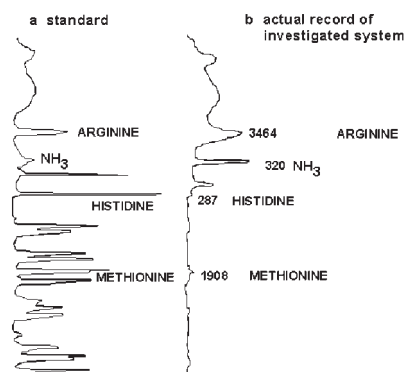


Fig. 1 HPLC spectrum of powder condensation product

The conversion process of the gaseous system CO₂-N₂-H₂O into the solid product containing abundant amino acids has been documented in [11]. Moreover the amino acids immediately condensed during their genesis into a macrostructure arrangement with a fractal structure on the microstructure level and being insoluble in water. Special analytical methods were chosen for identification of the species present in the products. Identification of individual amino acids in the solid product was performed by HPLC, when samples were dissolved using 6 M HCl applied at 100°C for 24 h.

Infrared (IR) absorption spectrometry was used for identification of the gaseous phases and their concentration changes. Analyses were performed in a 100 mm gas cell tube with KBr, CaF₂ or KRS5 windows. The gas cell discharge tube, consisting of a copper-wire stressed electrode and a brass, planar non-stressed electrode is described in more detail in Fig.1 of [10]. The gas cell discharge tube allowed us to prepare step-by-step measurements of the development in time of the gaseous products and intermediates formed by the high-voltage electric discharge from the inlet gas mixture CO₂-N₂-H₂O. The time intervals for investigation of the concentration changes are given in detail in [10], but were usually 1.5, 3.0, 4.5, 6.0 min. Both positive and negative polarities of the discharge were applied.

Solid products in the form of a fine powder with fractal microstructure were analysed by the KBr pellet technique. The samples were mixed with KBr in the ratio (0.2–1.0): 100 and pulverised in a vibration mill. The fine mixture was then compacted into a metal ring at 5–22 MPa. The pellets prepared in this way were used to obtain IR spectra by a scanning procedure.

The solid deposits on the electrode surfaces were analysed using IR reflection spectrometry by direct scanning of the surface layer. The quality of the IR reflection spectra depended on the wavenumber, incidence angle, reflection index and absorption. Two angles of incidence were available, 20 and 70°. Most of the reflection spectra were measured at 70°.

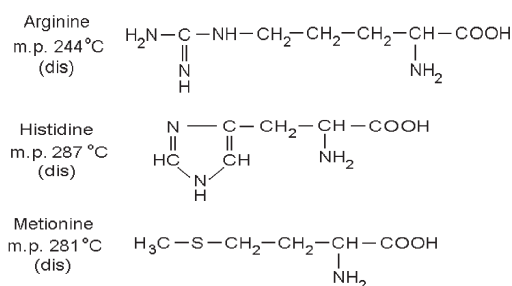
The high temperature isothermal decomposition of the amino acid samples in air was performed on a universal V1.9D TA instrument using its mass and differential

thermal analysers (MTA and DTA) to clarify the decomposition process and to find the combustible portion of the samples.

X-ray diffraction analysis of the amino acid products confirmed the amorphous character of the samples (CuK_α radiation, 40 kV, 20 mA).

Results and discussion

After conditioning the powder condensation product (obtained during conversion of the gaseous system CO₂(g)-N₂(g)-H₂O(g) in the electric discharge plasma inside the pilot equipment) in 6 M HCl at 100°C for 24 h the HPLC analysing method was applied. From the HPLC spectrum presented in Fig. 1 the following amino acids were identified:



All three amino acids occur with their terminal group -CH-COOH in an α-form arrangement,



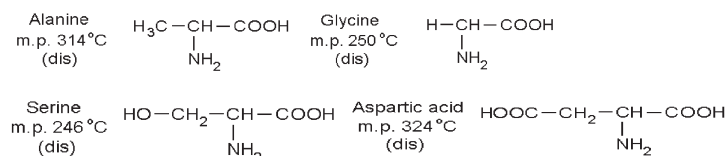
which can be easily changed into a terminal zwitterion, i.e., -CH-(COO)⁻, with groups -NH₃⁺



and -(COO)⁻. This can take place in the electric field of discharge system, on the non-stressed electrode in the case of positive polarity, or by interaction with water.

Important structural and molecular information could be established from the infrared absorption spectra of the powder condensation product using the KBr pellet technique. An important zone for identification is seen in Fig. 2.

In this way, with the help of measured reference spectra, the following amino acids were identified:



Again, the four amino acids exist with their terminal group -CH-COOH convertible to a zwitterion.



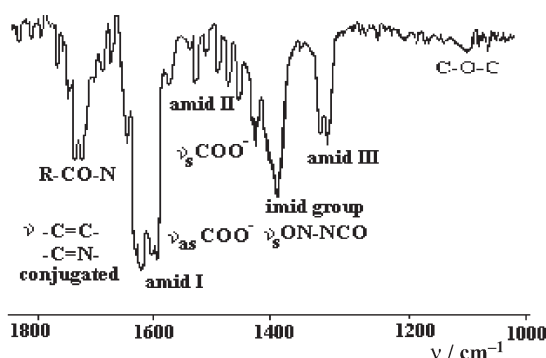


Fig. 2 Part of the IR spectrum used during analysis of individual amino acids

The amino acids mentioned are components of the powder condensate produced by a DC electric discharge. The condensation products are from oligo to polymer compounds. The condensate has a very low density, probably due to a fractal structure and a lot of holes as seen from micrographs (Fig. 10 in [11]). The individual amino acids are incorporated randomly in the polymer without any rules. X-ray diffraction showed the amorphous character of the polymer. IR spectra show that the polymer chains are highly branched and cross-linked, and contain a large number of amide groups, especially in the α position, and a variety of intra and intermolecular hydrogen bonds. This information about the product implies its proteinoid character in the sense described earlier by Oparin [14].

We have tried to compare our condensation product with the linear L-Ala-L-Ala-L-Ala complex described in [12, 13, 15]. For this comparison we have used information about the composition from IR spectra and the fact that solvent molecules (water) are an integral part of both our compound and the peptide structure inside a molecular complex.

A typical property of all condensed amino acid hydrates is their thermal instability. Figure 3 confirms that the dynamic thermal decomposition in air starts even below 100°C and ends with an intensive loss of mass between $290\text{--}320^\circ\text{C}$ connected with the dissociation of amino acids. Because this process is exothermic, it marks, at the same time, the beginning of combustion of the organic components present. The total loss of mass at 320°C is approximately 85%. On isothermal heating at 320°C , the loss of mass increased to 99%. The incombustible residue is CuO.

The difficulty experienced in dissolving the amino acids from their solid condensate (by boiling under pressure in 6 M HCl), is evidence of strong binding forces and cohesion in the condensate. The condensate can therefore be considered as a non-linear proteinoid with a high flexibility of peptide units [12, 13].

It is very important to understand the involved chemistry and energetic balance in the conversion of the gaseous mixture $\text{CO}_2(\text{g})\text{-N}_2(\text{g})\text{-H}_2\text{O}(\text{g})$ during final product formation. The process starts in the discharge zone by activation steps involving formation of an electronically excited metastable state of molecular nitrogen $\text{A}^3\Sigma_u^+$. This

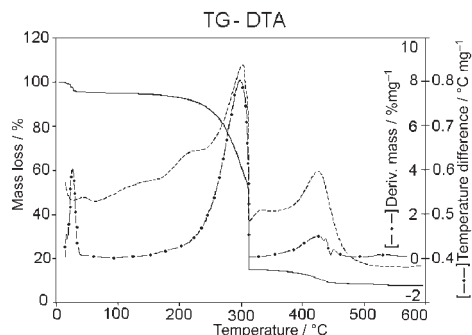


Fig. 3 Thermal analysis of the solid condensate of amino acids (TG, DTA, DTG)

excitation state can be achieved by electron, or repeated electron, impact with total energy of ~6.8 eV from the ground state X³Σ_u⁺ as we can see from Fig. 4 [16].

Activation is followed by the formation of energy-rich intermediate species, formation of catalytic spots on electrode surfaces, volume reactions under non-equilibrium plasma conditions, and surface reactions on electrodes, as explained below.

The energy of activated N₂ can be incorporated into CO₂, whereby the two most important radicals, NCO* and ON-NCO are generated. The space between the electrodes represents a drift, quench and clustering zone. In this zone many new intermediates and radicals are produced: H, OH, N, NH, NH₂, CH, CH₂, CH₃, NCO*, CN and others. Reactions between activated radicals, free-radicals and neutral intermediates follow after the activation in the same zone of the discharge. One of the most important is the free radical NCO*. It is a linear long-living species [17] contributing to fast reactions like:

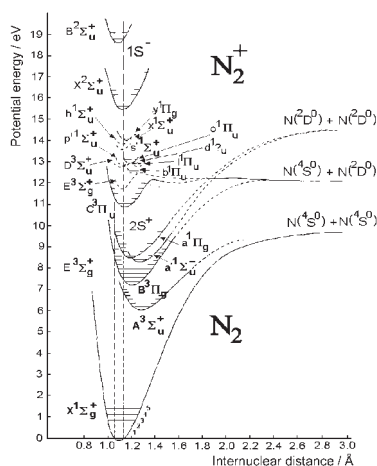
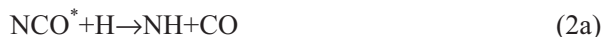
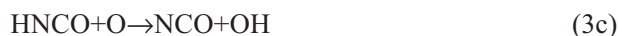
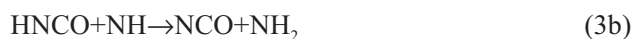
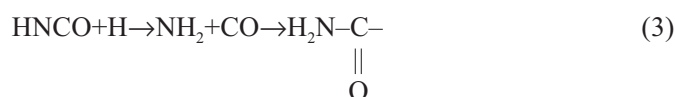


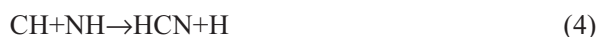
Fig. 4 The relation between potential energy and inter-nuclear distance for nitrogen



HNCO is a tetra-atomic, non-linear molecule with six internal degrees of freedom: the three interatomic distances: C–O, N–C and N–H, the two bending angles N–C–O and H–N–C and one out-of-plane angle. It also takes part in several reactions:



HCN can be produced directly, but also in the reaction



All reactions (2–4) take place under the non-equilibrium plasma conditions created in an electric discharge in the space between electrodes. A very important role is played by the reactions on the electrode surfaces. The basic volume and surface reaction pathways are illustrated schematically in Fig. 9 in [11]. The most important surface reactions are



To find out more about the surface reactions we have performed precise interpretation of reflection IR spectra from electrode surfaces (Fig. 5) for both polarities

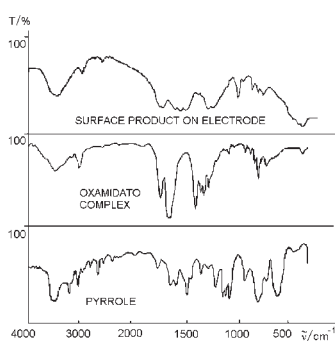
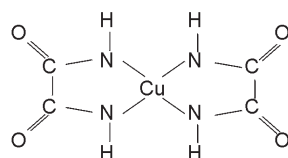


Fig. 5 A reflection IR absorption spectrum of the non-stressed electrode surface, an IR spectrum of an oxamidato complex from [18], and the reference spectrum of pyrrole liquid made for comparison on the same scale

of electrodes and discharge. For comparison we have scanned reference spectra of various compounds (Fig. 6) collected from databases.

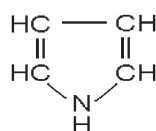
On the basis of the IR spectra, the following species were found to be attached to the electrode surface: H₂N-COO* (building block of polyurethanes), H₂N-CO* (building block of amides), oxamidato complex Cu(HNCO)₄, heterocyclic pyrrole, pyrimidine and similar rings and their oligomers.

The oxamidato complex is precipitated on both electrodes, but its attachment to the electrodes is different. The copper complex is attached to the negative polarised electrode through the positively charged central atom Cu^{nt}. Bonding with the positively polarised electrode occurs through the negatively charged oxygen atoms. Bonding of the Cu^{nt} ion of the copper complex with the negatively polarised electrode results in a change from a planar form to a square pyramidal arrangement (the copper atom is shifted out of plane of the organic part) and in labilisation of the N-H bonds. In this way, the hydrogen atoms can break away more easily.



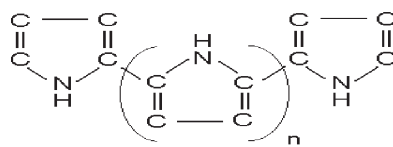
oxamidato complex

From the IR spectra in Fig. 5 evidence is clearly seen of the existence of pyrrole molecules (I) in the system on a non-stressed electrode. The molecule is photosensitive and can take part in condensation processes.



pyrrole (I)

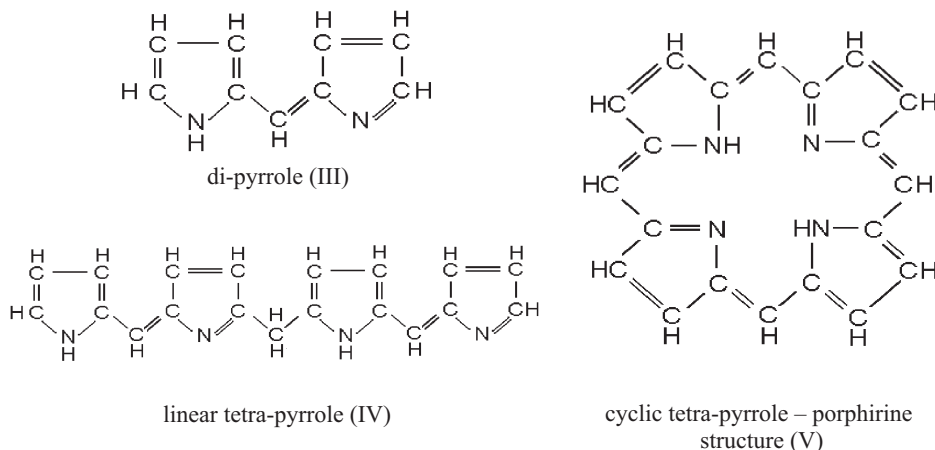
One of the products described in literature on the production of polypyrroles is the linear polymer (II). This polymer II demonstrates metallic conductivity, but is not present in our systems.



polymer (II)

The condensation of the pyrrole ring occurs after insertion of a -CH= group (structure III), followed by dimerisation to form the linear structure IV, or cyclisation to form the cyclic molecule V. The molecule resembles the porphyrin cyclic mole-

cule, a well-known catalyst. The evidence for such a compound is an important feature of the reacting assemblage of products, which shows a constituent probably capable of contributing to the formation of the basis for prebiotic photosynthesis.



Conclusions

- The energetic balance in the conversion of the gaseous mixture CO₂(g)– N₂(g)– H₂O(g) into a solid condensate of amino acids in a high-voltage, direct-current, electric discharge is very favourable. The conversion proceeds through energy steps starting from the excitation state of molecular nitrogen A³Σ_u⁺. This excitation state can be achieved by using electron impact or repeated electron impact with total energy of ~6.8 eV for transition from the ground state energy X³Σ_g⁺ as can be seen from Fig. 4 [16]. The energy of activated N₂ can be incorporated into CO₂, whereby the two most important radicals, NCO* and ON–NCO are generated.
- The participation of the NCO* radical in fast chemical reactions is presented in reactions (2a)–(2c).
- The thermal dissociation of the N–N bond in nitrogen needs an energy of 9.85 eV. This high energy barrier can be overcome by application of the excitation to the electronic state N₂*A³Σ_u⁺.
- The excitation energy of the electronic state and the formation of the active radicals NCO*, ON–NCO, HNCO, H, OH, N, NH, NH₂, CH, CH₂, CH₃, CN can be substantially recovered by the condensation energy of amino acids.
- The amino acids produced can be used as a new nitrogen-containing organic fertiliser. The fixation of nitrogen has unlimited raw material reserves. Application of the new process might help to solve in decreasing excess CO₂ without limiting industrial production and development.
- This work has a close connection with prebiotic chemistry connected with the origin of life using electric discharge as an activation factor as was described by Miller in [19].

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