

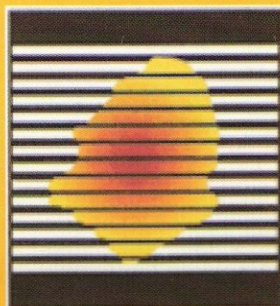
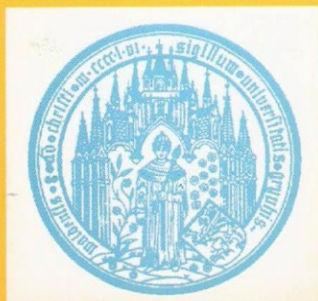
M. MORVOVA

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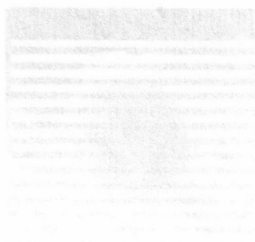
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CONVERSION OF THE GASEOUS SYSTEM $\text{CO}_2\text{-N}_2\text{-H}_2\text{O}$ INTO A SOLID MIXTURE OF AMINO ACIDS USING ELECTRIC DISCHARGE AND HETEROGENEOUS CATALYSIS OF ELECTRODES

Marcela Morvová, Imrich Morva, František Hanic, Zdenko Machala, Mário Janda

*Institute of Physics, Faculty of Mathematics and Physics, Comenius University,
Mlynská Dolina F2, 842 48 Bratislava, Slovakia, e-mail: morvova@fmph.uniba.sk*

ABSTRACT

We present here the conversion of combustion exhaust or at least $\text{CO}_2\text{+N}_2\text{+H}_2\text{O}$ gaseous mixture into solid amino acid condensate (95% of the product) in an spontaneously pulsing direct-current electric discharge operating in a corona geometry. The synergetic effect of heterogeneous catalysis on the metal organic part of the product formed on the non-stressed electrode (5% of the product) was responsible for the specific character of the discharge and products.

The final product of the process is a powder with a fractal structure on the microscopic level with low specific weight, insoluble in water. The product was analysed using IR absorption spectrometry, microscopic and SEM photography, HPLC, thermogravimetry and X-diffraction. The following amino acids were observed in the final product: alanine, serine, glycine, aspartic acid, lysine, arginine, methionine, histidine.

The method provides a contribution to CO_2 and combustion exhaust utilisation, which is present together with nitrogen fixation. The carbon dioxide conversion is as high as 40- 65%. The co-effect NO_x and CH_x removal was up to 95%.

The gas cleaning process may also contribute to explanation of the origin of life on Earth, because it represents the modified Miller experiment [1], which better correspond to the natural return stroke of lightning into water. In such case sublimation of minerals from sea bottom create due to interaction with spark similar compound as are in our case on electrode surface and correspond to the effects described by L.E. Orgel in [2].

INTRODUCTION

Up to 85% of all forms of energy (electricity and heat production, industry and transport) is produced in combustion processes. Much of the current concern about the fate of the global environment is related to the increased concentration of greenhouse gases, because they trap infrared radiation. Carbon dioxide is the most important greenhouse gas. To protect the climate and ecosystem for present and future generations it is necessary to reduce the present emission level of CO_2 , as was agreed in Kyoto (1997). This was the reason for focussing our attention on the creation of multifunctional discharge equipment for combustion exhaust cleaning connected with CO_2 utilisation and nitrogen fixation.

EXPERIMENTAL

A spontaneously-pulsing streamer to spark transition-type of electric discharge, supplied by a d.c. high voltage source was used. The discharge operates in corona geometry, but some physical properties correspond to a high-pressure glow discharge. The discharge has strongly shining channels migrating quickly along the stressed electrode. The individual sparks

appeared regularly with repetition frequency of several kHz. The discharge comprises also surface discharge around the formed spots on non-stressed electrode surface.

For *in situ* step-by-step time development measurements, kinetic and material studies, the gas cell corona discharge tube was developed and used as described elsewhere [3].

Additionally the multifunctional discharge system (24 discharge tubes) developed for tests on a pilot scale with a gas flow volume of 50-100 Nm³/hour was used. The reactor was put into the by-pass gas flow or in a full-size exhaust source. A high-voltage dc source of both polarities up to 20 kV, maximum power 500 W and maximum current 30mA, was applied for discharge generation. On-line diagnostics, using isokinetic sampling followed by the gas chromatography, mass spectrometry, total carbon measurement, IR absorption spectrometry, chemiluminescence and electrochemical methods and magnetic susceptibility (for O₂) analysing methods. The system produces larger amounts of solid condensation products necessary for its detailed analysis of product. For solid samples the KBr pellet technique of IR absorption spectrometry and high precision liquid chromatography (HPLC) were used to estimate the individual amino acids. The high temperature isothermal decomposition using its mass and differential thermal analysers (MTA and DTA) to clarify the decomposition process and to find the combustible portion of the samples was used. And finally X-ray diffraction analysis of to confirm the amorphous character of the samples (CuK α radiation, 40kV, 20mA) was used. The electrode surface from the discharge system was analysed using IR reflection spectra, with 20° and 70° angles of incidence.

RESULTS AND DISCUSSION

The main source of combustion exhaust used for gas cell measurements was produced in combustion calorimeter and were enriched by various components as NO, NO₂, CH₄, CO, CO₂ to cover the most usual composition of exhaust. To know how reducing species influence the time development of products the alternative the oxygen poor-rest fuel rich exhaust was produced from fuel (CH₄)-air by its combustion inside discharge as described elsewhere [4].

In gas cell discharge tube was used for step by step time development measurements of gas phase products and intermediates formed by discharge in introduced gas mixture. The infrared spectra were scanned from the area of inter electrode distance *in situ*. First the IR spectrum of introduced gas was scanned. Then the discharge was applied for a defined time and again the spectrum was scanned. This procedure we have reiterated till no more changes in composition of the gas take place. The relative concentration changes in percentage of input concentration for both polarities of discharge are seen Fig.1

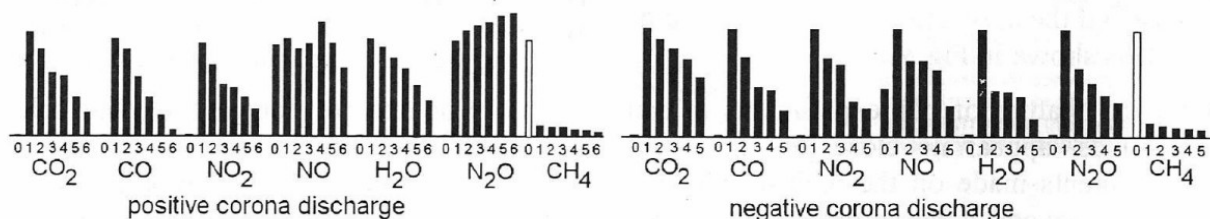


Fig.1 The time development (in one minute intervals) of relative concentration changes of each component of a methane-air-NO_x mixture combusted by the discharge, in percentage of the first-minute concentration, due to positive and negative discharge action

An important information from gas cell measurements is the spectroscopic evidence about formation of -NCO stable intermediate radical from the minority gas analysis as seen of Fig.2

The presence of -NCO radical in gas after discharge is seen from detailed IR absorption spectrum (bands in gas phase are at 2270 and 2290 cm^{-1}). From spectra of gas products we see also the rich variety of gaseous reaction products and stable radicals formed especially in positive polarity. The development of these products is based on radicals formed by the discharge, as are: -NCO , -NH_2 , -CH_2 , -COO^\cdot , ON-NCO and OC-NCO in cis configuration. Similar radicals are formed from nitrogen combustion components in rich hydrocarbon flames [5]. On the other hand, the compounds built on the basis

of NCO , namely HNCO , are used for quick and effective NO_x removal from combustion exhaust [6].

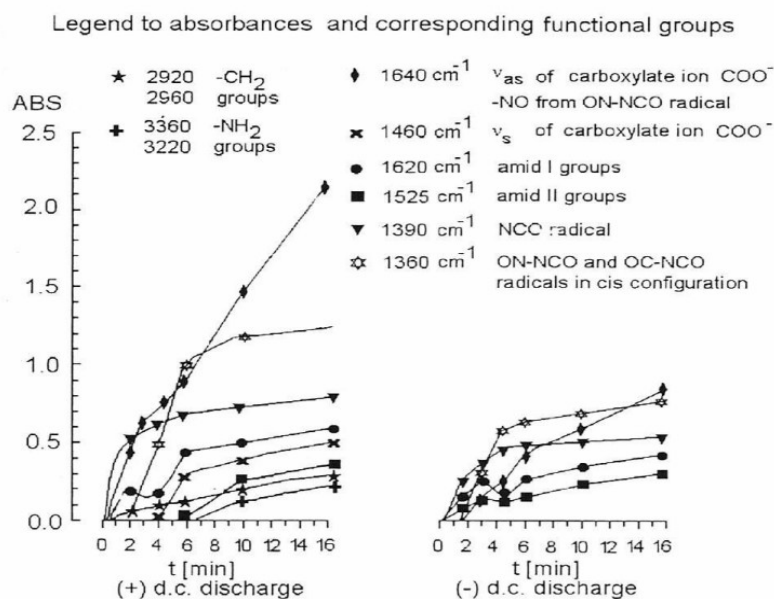


Fig.2 The time development of minority products, as the extinction coefficients are unknown, measurements are based on IR absorbances

After finishing of gas phase measurements the plate non-stressed electrode was chosen out from the gas cell discharge tube and the reflection IR absorption spectrum of it was scanned out. From IR reflection spectra, the presence of oxamidato complexes with known ferroelectric properties [7] and oligo pyrrole type of compounds with probable catalytic activity can be seen. It is known that linear and cyclic tetrapyrrole compounds are important parts of photosynthetic chromophores (linear phycocyanine, cyclic chlorophyll) [8]. Comparison of the IR spectrum of the non-stressed electrode surface and the absorption spectrum of liquid pyrrole is shown in Fig.3.

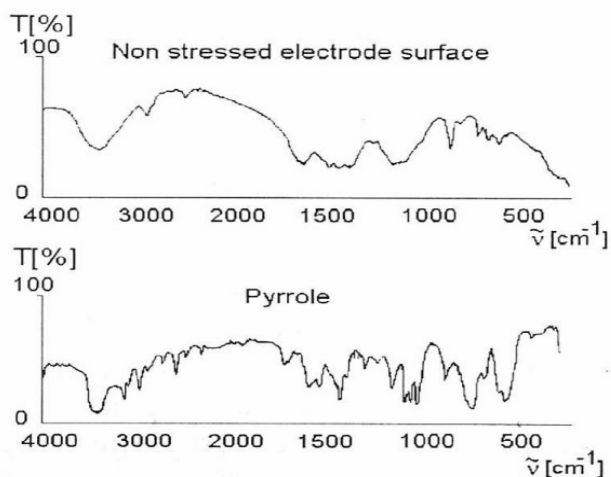


Fig.3 Comparison of the IR reflection spectrum of a brass metal non-stressed electrode surface containing oxamidato complexes and pyrrole-ring based structures, with the IR spectrum of pyrrole liquid

A typical feature of our experiments is that the final products are not gaseous, but solid compounds appearing close to the surface of electrodes. From various groups of measurements made on the multi-discharge system we have prepared solid product in the amount of several hundred grams. Such amount was necessary to provide various groups of measurements. From thermogravimetric analysis we know that about 95% of the product is a powder of amorphous amino acid condensate and 5% is an metal organic compound bonded to the surface of the electrode with catalytic properties. The powder product is a statistical polycondensate, containing the amino acids, arginine, histidine, methionine (estimated by HPLC), lysine, glycine alanine, serine, and aspartic acid (estimated by comparing IR absorption spectra of product and pure amino acids).

CONCLUSIONS - SCIENTIFIC ASPECTS

The involved chemistry till final product formation can be divided into three important steps:

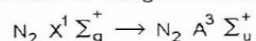
1. activation by electric discharge and heterogeneous influence of electrode surface,
2. formation of energy-rich intermediate species, formation of catalytic spots on the electrode surfaces, volume reactions under non-equilibrium plasma conditions, surface reactions on the electrodes,
3. final product formation due to polycondensation process close to the non-stressed electrode surface, setting free of water and oxygen in condensation process.

The most important activation step is the excitation of N_2 to metastable state $N_2A^3\Sigma_u^+$ formed by repeated electron impact in discharge with energy close to 6.5eV [9]. The lifetime of this state varies between 1.3-1.9 s [9,10], what increases its probability to participate in chemical reactions. The second important activation step is water dissociation on electrode surface. The N_2 activation step is followed by its incorporation into CO_2 , to form two of the most important active radicals, namely ON-NCO and -NCO. This step in reality begins the nitrogen fixation process, one of the most important process involved in the origin of life on Earth. The development of all further products is based on reaction of -NCO (linear amino acids) and ON-NCO (heterocyclic compounds) radicals. An overview of the processes taking part in an electric discharge going on in a combustion exhaust is given in Fig.4.

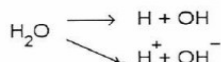
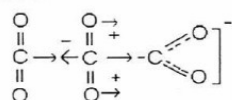
Combustion exhaust reactions in electric discharge - formation of amino acids

Activation processes on main combustion components

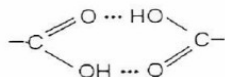
formation of electrons in discharge
activation of nitrogen in discharge



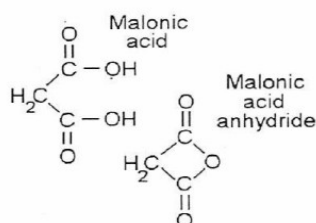
dissociation and/or dissociative ionisation of water on electrode surface spots with enhanced dielectric constant at favourable energies

deformation of carbon dioxide
in electric field

influence of water - formation of cyclic dimer of carboxylic acid

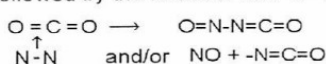


formation of

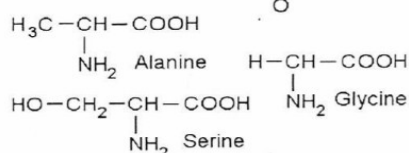
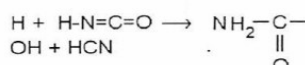
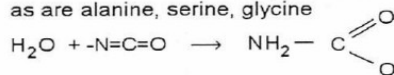


Volume reactions in discharge

activation by $N_2 A^3 \Sigma_u^+$
followed by the reaction with $O=C=O$



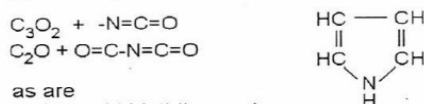
in reaction with water simple amino acids
as are alanine, serine, glycine



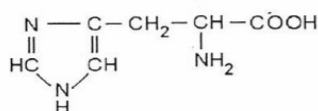
radicals



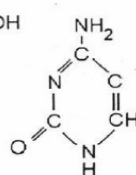
react with malonic acid anhydride creating pyrrole ring based amino acids



as are
amino acid histidine and



and DNA base cytosine

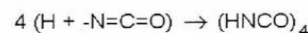


Reactions on electrode surface

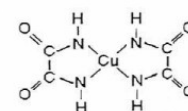
Due to later described processes catalyst with enhanced dielectric constant is formed on electrodes

Dielectric spots increase the number of formed microsparks and in this way also grows the flow of energy to the electrode surface

Surface reaction on copper

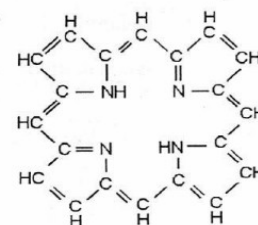


developes to the formation of



oxamidato complexes

These complexes are in reaction with malonic acid (and anhydride) spontaneously converted into cyclic tetrapyrrole structures as porphyrines, the bases of life important chromophores



Due to the influence of the electric field, CO_2 is deformed into a carboxylate ion. By reaction of the carboxylate ion with water, a cyclic dimer of carboxylic acid is formed and finally dicarboxylic acids (malonic, succinic) and hydroxy acids (apple, citric and tartaric), what we have in details studied elsewhere [11]. Further development of products can lead to the formation of sugar and lipids.

Quenching of active species takes place in the electric field inside the drift zone of the discharge and leads to the formation of clusters, and finally polycondensation of amino acids, together with other products, into amino acid condensate of proteinoid character and is seen from the Fig.5.



Fig.5 Microscopic photograph of solid product; magnification on left side 150 in middle 500 and on right side SEM photograph with magnification 8000; the smallest particles on right side are about 1 μm

Oxamidato complexes (having enhanced dielectric constants) are the predominant compounds on the anode and participate in the catalytic effects of the anode. The reaction with C_3O_2 (decomposition product of $\text{CO}_2 \rightarrow \text{CO} \rightarrow \text{C}_2\text{O} \rightarrow \text{C}_3\text{O}_2$) on the electrode surface in the presence of water, leads to the formation of cyclic tetrapyrrole-ring based products. The pyrrole-ring based compounds are the bases of life-important pigments (cyclic terapyrrole pigment with central atom Mg = chlorophyll, linear terapyrrole pigment with central atom Cu = phycocyanine). Pyrrole-ring-containing amino acid histidine and RNA bases such as cytosine and uracyl are formed on the electrode surface by splitting from the metal organic product.

The early oxygen free primary atmosphere consisted mainly of gases released by volcanic activity similar to the composition of today combustion exhaust as described in [1] i.e. CO_2 , CO , H_2O , N_2 , small amounts of NH_3 , H_2 , CH_x .

CONCLUSIONS - APPLICATION ASPECTS

The observed carbon utilisation efficiency in the multifunctional discharge systems described above is high (40-65% of CO_2 is utilised). The energy consumption for conversion of 1 m^3 of the gaseous mixture $\text{CO}_2\text{-N}_2\text{-H}_2\text{O}$ into amino acid condensate is 2.3-4.7 Wh/m^3 , i.e. 8.3-16.9 kJ/m^3 .

REFERENCES

- [1] Miller, S.L., A Production of Amino Acids Under Possible Primitive Earth Conditions: Science 117 (1953), p. 528-529
- [2] L.E.Orgel Orig. Life Evol. Biosphere 28 (1998), Polymerization on the Rocks: Negatively-Charged α -Amino Acids, pp. 235-243
- [3] Morvová, M., J. Phys. D: Appl. Phys., 31 (1998) 1865
- [4] M. Kurdel, M. Morvová: DC corona discharge influence on chemical composition in mixtures of natural gas with air and its combustion exhaust with air, Czechoslovak Journal of Physics, Vol. 47 (1997), No. 2, pp. 205-215
- [5] Pershing, D.W., Windt, J.O.I., 16th Symposium on Combustion, The Combustion Institute, Pittsburg, PA, (1977) 389
- [6] Perry, R.A., Siebers, D.L., Nature (London), 324 (1986) 657
- [7] Ambalangodage Champa Jayasuriya, Shigeru Tasaka, Norihiro Inagaki, Physics Express Letters, J Phys. D: Appl. Phys., 28 (1995) 1534
- [8] Glaser, A.N., Ann. Rev. Microbiol., 36 (1982) 173
- [9] Lofthus, A., Krupenie, P.H., J. Phys. Chem. Ref. Data, 6 (1977) 113
- [10] Magne L., Cemogora G., Veis P., J. Phys. D: Appl. Phys., 25 (1992) 472
- [11] M. Morvová, Czech.J.Phys. Vol.49, No.12 (1999), pp. 1703-1720