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REMOVAL OF AROMATIC RING BASED VOC USING ELECTRIC DISCHARGE AND ELECTRODE CATALYSIS

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Abstract

For removal of aromatic Volatile Organic Compounds (VOC) such as benzene (C_6H_6), toluene ($C_6H_5CH_3$), xylene ($C_6H_5(CH_3)_2$) styrene ($C_6H_5CHCH_2$) and ethyl benzene ($C_6H_5CH_2CH_3$) we have used the spontaneously pulsing electric discharge with „brush-like" streamer in transition to spark regime feeded by dc HV source.

Following changes on aromatic ring were found out. In first step the CH_3, CH_2, ethyl or vinyl groups are from ring removed The benzene ring is then oxidised to quinone. Next oxidative step opens the ring and creates malonic acid from the ring fragments. This intermediate can further react with water and/or NCO radical based structures to create heterocyclic nitrogen containing pyrrole, pyrimidine and/or similar ring.

On this bases amino acid histidine, DNA base cytosine and some linear oligo pyrrole compounds were formed on the electrode surface. These components were not prepared till now in synthetic way and its creation seems to play important role during formation of life in pre-biotic Earth.

Introduction

Aromatic Volatile Organic Compounds (VOC) such as benzene (C_6H_6), toluene ($C_6H_5CH_3$), xylene ($C_6H_5(CH_3)_2$) styrene ($C_6H_5CHCH_2$) and ethyl benzene ($C_6H_5CH_2CH_3$) are exhaust gases with enhanced toxicity on human body comparing to other VOC. Usually these compounds after introducing of energy during combustion process are only partially into CO_2 and H_2O, but create PAH and/or soot, which are usually also toxic.

In the non-thermal plasma processes the energy is directed preferentially to the electron impact dissociation and ionisation of the background gas to produce reactive radicals. These radicals participate in decomposition of the targeted VOC. Silent discharge plasma has been successfully applied to the removal of toluene at lower concentrations [1]. Complete toluene destruction has been obtained in the packed bed and the nanosecond pulsed corona reactors [2]. The electron beam irradiation of various VOC including xylenes lead to high removal efficiency for single compounds at low concentrations [3]. The silent discharge technique has been also applied to several VOC including benzene with the maximal efficiency for high VOC concentrations [4].

The aim of most of the authors is to decompose the VOC to intoxic gaseous CO_2 and H_2O, but nowadays it seems to be less attractive, since CO_2 is a major contributor to the Earth's greenhouse effect. However, some products in the form of solid phase often appear on the reactor electrodes in various discharges. The aim of our experiments is to convert VOC to non-toxic solid products and at the same time to decrease the CO_2 production.

Experimental

For the purpose of the benzene ring based VOC removal a spontaneously pulsing d.c. electric discharge with „brush-like" streamer to spark type of current pulses feeded by dc HV source was used. As a high voltage source for this electric discharge a transformer with ferrite core was used. The repetition frequency of the switching power source was 33 kHz. The individual sparks appeared regularly.

The discharge operates in corona geometry, but some physical properties correspond to the high-pressure glow discharge. The cathode and anode spots are fully developed in the near electrode region. The discharge has strongly shining channels migrating quickly along the stressed electrode.

The discharge chamber consists of the copper rod with an internal thread (stressed electrode) and coaxial brass cylinder (non-stressed electrode) with inter electrode distance of 6mm. The length of the discharge tube is 50 cm. The synergetic effect of electrode surface catalysis was also present.

The vapours of benzene ring based compounds were decomposed in a corona discharge plasma generated under atmospheric pressure in the experimental gas flow system presented together with electric schema and discharge gap in Fig.1. The carrying gas was air applied from the pressure tank. The airflow was controlled by two flow meters and had the values up to 20 l/min in flow meter 1 and 2 m/s in flow meter 2. The carrying gas was enriched with studied VOC to saturated vapour pressure at 20°C for benzene and to saturated vapour at higher temperatures up to 120°C for toluene, styrene, ethylbenzene and xylene to reach concentration at least 3 000 ppm. The total gas flow was close to 22 l/min. It corresponds to the flowing velocity of about 1,4 m/s and residence time of 0,3 s in the discharge chamber.

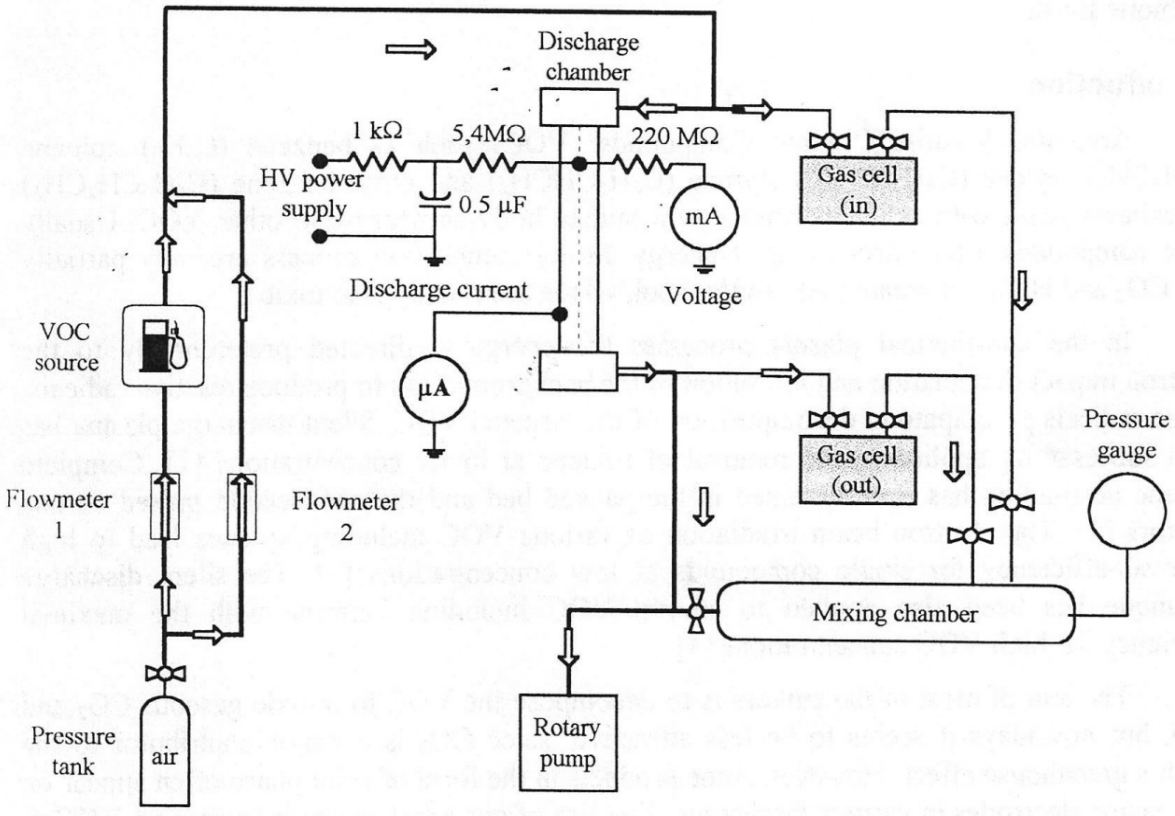


Fig 1 Experimental gas flow system together with electric schema and discharge gap

The infrared absorption spectroscopy was used as the diagnostic method. The spectra were obtained using IR spectrometer SPECORD M 80 working in the far, middle and a part of near infrared region (4000-200 cm^{-1}).

The 10cm gas cells with KBr windows were used for gas analysis. For solid samples the KBr pellet technique was used. The electrode surface was analysed using reflection spectra. The used device allows to measure the reflection spectra at 20° and 70° angles of incidence. Most of the spectra were measured with 70° angle as is seen from Fig 2.

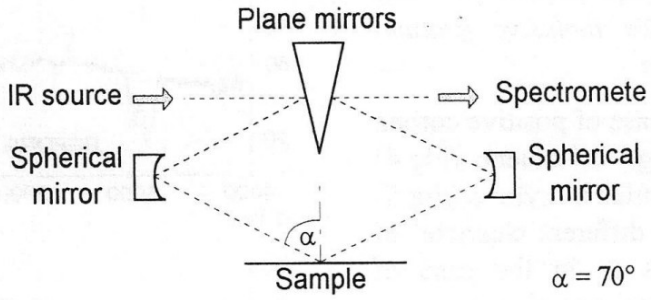


Fig.2 IR reflection equipment

To improve the removal process we have introduced water vapour using various spraying systems producing microscopic water droplets. Measurements with water presence confirmed the assumption that important reaction accelerating species is OH radical.

Results and discussion

The influence of discharge on benzene ring based VOC can be seen in 3 groups:

1. benzene (ring without substituent),
2. toluene, ethyl benzene, xylenes (ring with saturated substituent),
3. styrene (ring with unsaturated substituent).

We present here the IR spectra of gas phase, where we can see the efficiency of removal process for:

- air plus benzene and both polarity of discharge on Fig.3,
- air plus toluene and both polarity of the discharge on Fig.4,
- air plus xylene and both polarity of the discharge on Fig.5.

The removal efficiency of benzene was for positive polarity 64% and for negative polarity 87%. CO and CO_2 are not present in gas products.

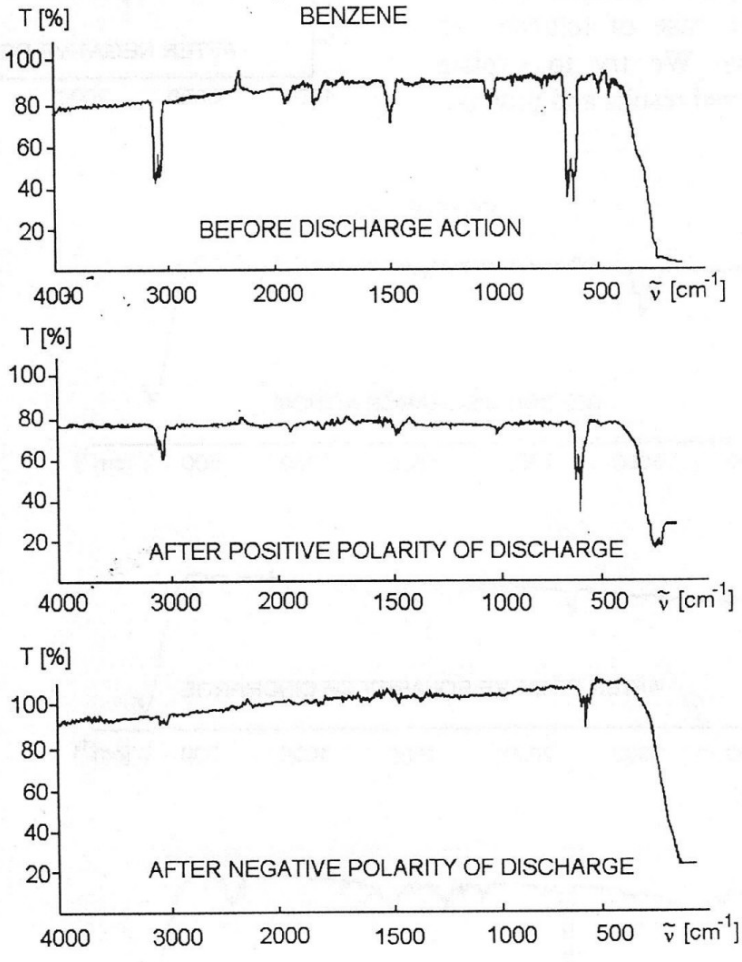
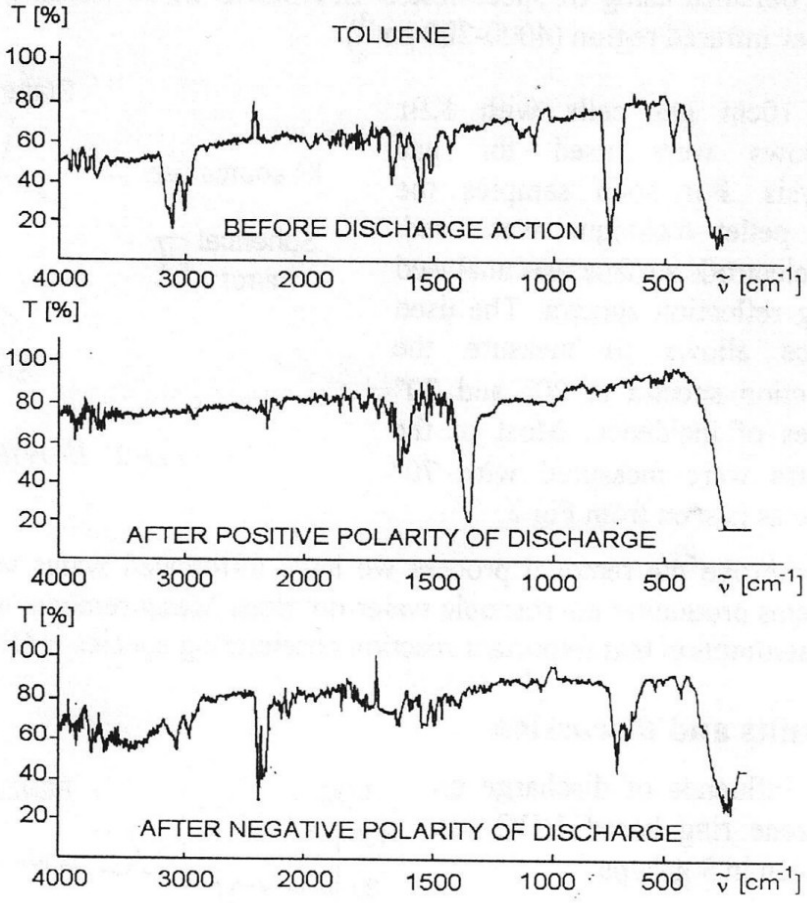


Fig.3 Action of discharge on air plus benzene for both polarities inclusive product analysis

Fig.4 Action of discharge on air plus toluene for both polarities inclusive product analysis →



In the case of positive corona discharge in toluene (Fig.4) and similar in xylene (Fig.5) is seen different character of changes as in the case of discharge negative polarity. From all gained spectra on Fig. 3, 4, 5 is seen the voluminous decrease of -CH_x groups concerning to the band at ~3040 cm^{-1}. The CO and CO_2 concentrations are very small (<1%) in positive polarity, but are significant in negative polarity (~12%) in the case of toluene and xylene. We try to explain observed results and propose

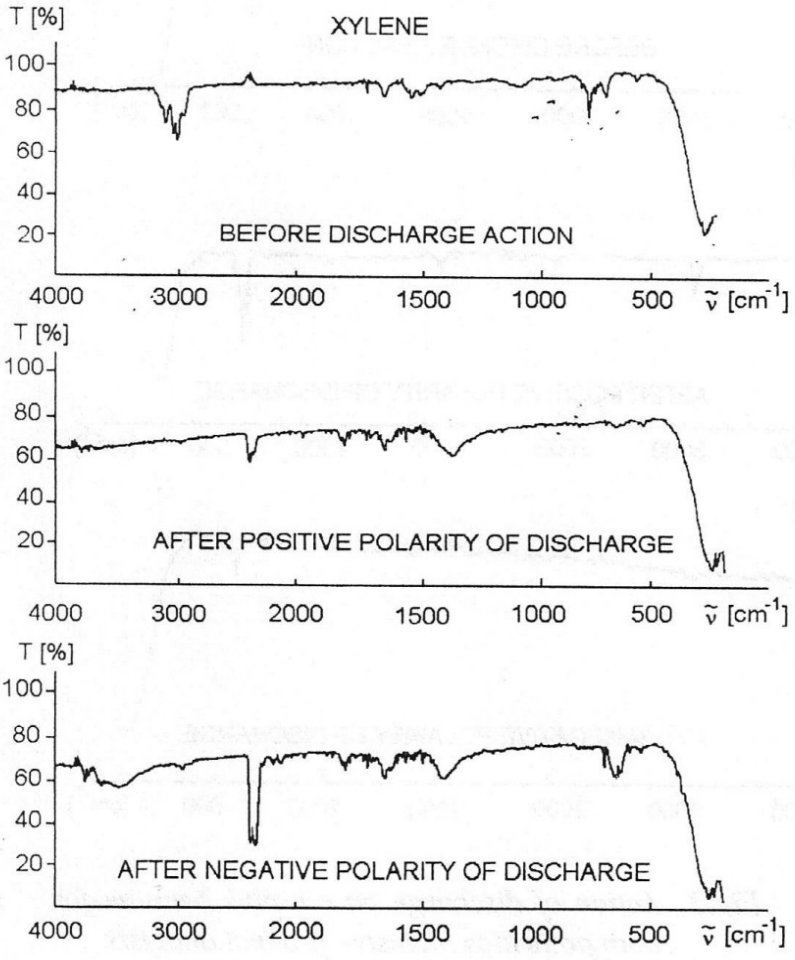


Fig. 5 Action of discharge on air plus toluene for both polarities inclusive product analysis

the destruction of benzene ring into malonic acid. A presence of activated nitrogen in discharge zone leads to formation of -NCO and ON-NCO radicals. These radicals react with ring fragments containing malonic acid and form heterocyclic compounds similar to pyrrole ring. After reaction with water stable amino acids are formed. The removal efficiency of xylenes in positive polarity is 86% and in negative polarity is 94%. In positive polarity the benzene ring decomposes into malonic acide and one

larger fragment together with ring substituent, in negative polarity the substituents are removed from ring prior its decomposition. This leas to formation of CO_2, CO, water and alcoholes after oxidation of these fragments as it is seen in the case of negative discharge polarity. Decomposition of styrene goes on with very high efficiency (95-99%) because it is connected with radical induced copolymerization of input styrene with formed products. These processes are in more details described in our previous work [5].

A typical feature of our experiments is that the major products are not gaseous CO_2 and H_2O but solid and or liquid compounds appearing close to the surface of electrodes. The IR spectra of products from electrodes confirm the formation of amino acids and heterocyclic unsaturated compounds due to presence of amide I, II, III bands (wave numbers 1700-1655, 1565-1400, 1300 cm^{-1}) as seen in Fig.6. This indicates molecular nitrogen and/or NO_x fixation into the product.

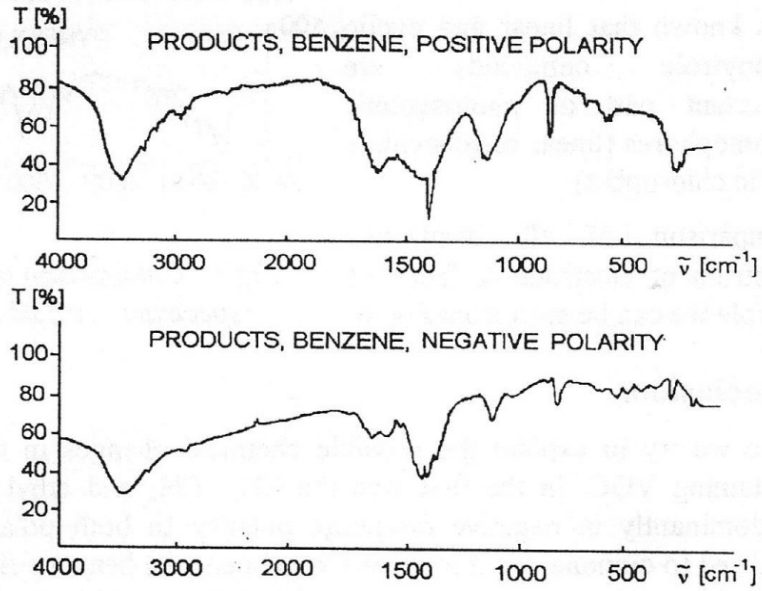


Fig.6 Final solid/liquid products from air-benzene mixture after discharge action

The product is statistical polycondensate containing amino acids arginine, lysine, histidine, methiodine, glycine and other. This information was gained by comparing of product IR spectra with calibration IR absorption spectra of pure components and also from HPLC analysis. In the case of benzene decomposition in positive polarity discharge DNA base cytosine was very surprising but important component of product. The calibration IR spectra of most probable components of product arginine, histidine, lysine and cytosine are in Fig.7.

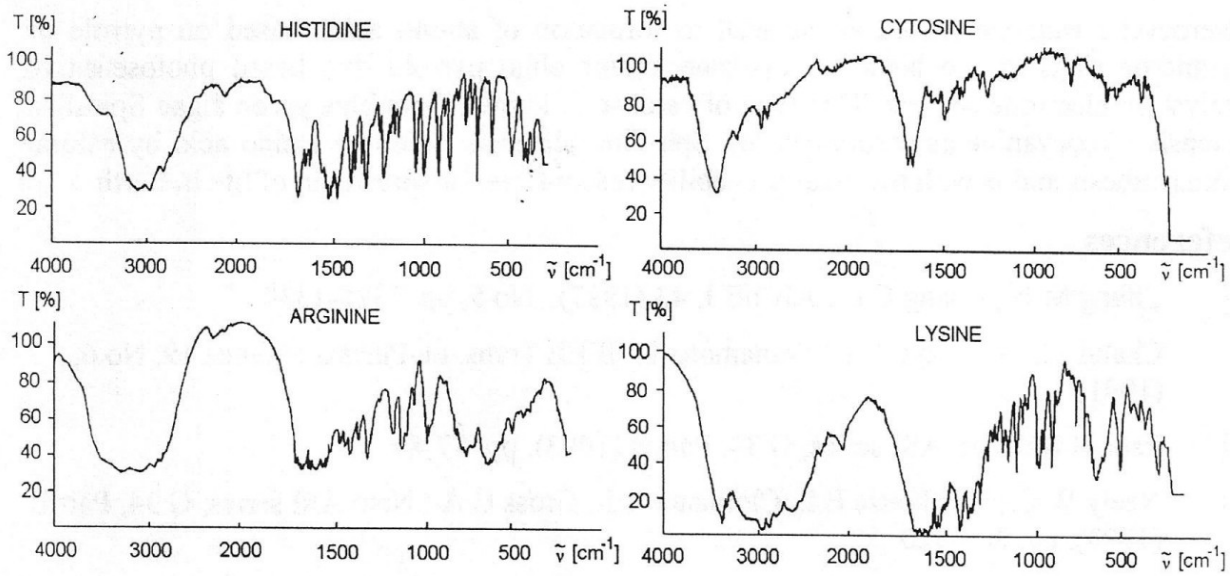


Fig.7 IR absorption spectra of histinine, arginine, cytosine and lysine

Precise analysis of non-stressed electrode surface by IR reflection spectrometry gave us more detailed information about functional group present on electrode surface.

From such spectra was found out that oxamidato complexes with published ferroelectric properties and oligo pyrrole type of compounds with probable catalytic activity were present.

It is known that linear and cyclic tetrapyrrole compouds are important part of photosyntetic chromophores (linear phycocynine, cyclic chlorophyl).

Comparison of IR absorption spectrum of electrode surface and pyrrole we can be seen from Fig. 8.

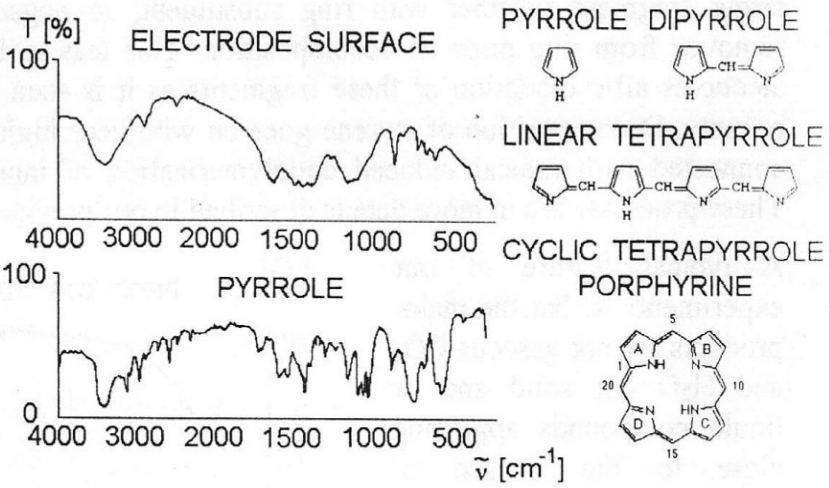


Fig.8 Comparison of electrode surface reflection spectrum with IR spectrum of pyrrole liquid

Conclusions

Here we try to explain the possible chemical changes in the mixture of air-benzene ring containing VOC. In the first step the CH_3, CH_2 and ethyl groups are from ring removed predominantly in negative discharge polarity In both polarities the benzene ring is then oxidised to quinone. Next oxidative step opens the benzene ring and creates malonic acid and in positive polarity also higher then C3 carbon number fragments. A presence of activated nitrogen in discharge zone leads to formation of -NCO and ON-NCO radicals. Formed intermediate fragments from benzene ring can further react with:

- Water to create hydroxy acids
- CO_2, CO and CH_x and water to create higher dicarboxylic acids
- NCO radical and water to create linear amino acids or to be closed into 5-6 member heterocyclic ring with one nitrogen hetero-atom
- ON-NCO radical to crate intermediate, which create linear amino acids with two NH_2 groups or is closed to 5-6 member heterocyclic ring with two nitrogen hetero-atoms

Heterocyclic ring mentioned above lead to formation of amino acids based on pyrrole or pyrimidine rings as are histidine, cytosine and/or oligo pyrrole ring based photosensitive catalyst on electrode surface. This type of catalyst is known from blue green algae Spirulina platensis (fycocyanine as chromophore). Spirulina platensis produces amino acid by natural photosynthesis and is with the great probability responsible for spread out of life in Earth.

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