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Plasmochemical Synthesis of Optically Active Substances

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***Abstract*— This work is devoted to the study of optical activity (rotation of the polarization plane of light by matter) of organic synthesis in a plasma–liquid system with a rotating gliding discharge submerged in a liquid. The initial reagents of synthesis were ethanol, ammonia, and CO_2. The possibility of plasma–chemical synthesis of an optically active substance when all the starting reagents are not active in the synthesis is shown.**

***Index Terms*— Chirality, CO_2, plasma–liquid system, polarimetry, rotating gliding discharge, synthesis.**

I. INTRODUCTION

FOR all 50 years of the intense development of plasma chemistry, one of its main focuses was on the synthesis of both organic and inorganic compounds. Plasma-activated synthesis allowed the production of new, unknown to conventional chemistry, nanomaterials, such as fullerenes and nanotubes. However, similar to conventional chemistry, the problem of induced enantioselective synthesis of chiral substances from nonchiral substances remains unsolved in plasma chemistry. The solution to this problem is much sought after, as the chiral synthesis is required to produce a wide range of biomedical drugs [1], [2]. An object is called chiral if it cannot be superposed on its mirror image. The term chirality is derived from the Greek word "hand" and was introduced into the scientific lexicon by Lord Kelvin. Chiral objects include molecules that contain an asymmetric carbon atom, e.g., amino acids and sugars. This means that these molecules have chiral properties when the central carbon atom is bonded with four different types of attachments (ligands) (see Fig. 1). Mirrored isomers (enantiomers) of such molecules are usually called "left" and "right" isomers and are marked in biophysical literature by letters L ("laevo"–left) and D ("dextro"–right). Mirrored isomers are interesting in that compounds that are composed of only L or only D isomers (e.g., solutions and crystals) have identical physical properties: the same internal energy, solubility, melting and boiling temperatures, and so on. Their only physical difference is that these compounds rotate the polarization plane of the light that passes through them in opposite directions; namely, they have opposite optical activities [3].

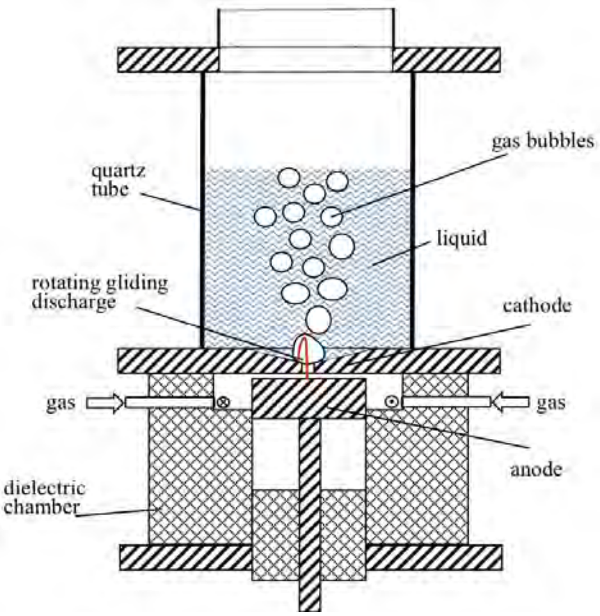

Fig. 1. Experimental setup with rotating gliding discharge submerged in liquid.

The general rule of organic chemistry states that optically inactive reactants yield optically inactive products, or more specifically, the synthesis of the chiral compounds from achiral reactants always yields a racemic modification, that is, a mixture composed of the equal amounts of compounds with opposite optical activity [1]. The solution to this problem can have a significant impact on plasma applications in agriculture, plasma medicine, pharmacology, the food industry, and so on.

Organic chemistry commonly extracts the substance with the specific chirality from the racemic mixture by using homochiral substances obtained from living organisms. The products of the reactions between R and L enantiomers and exclusively right-handed substance R' (diastereoisomers R-R' and L-R') are not mirror images of each other. Therefore, they have different physical properties, such as solubility in water, and can be separated.

One of the reasons that can explain the absence of the induced chirality in the conventional chemical synthesis pertains to the equal probability of the different movement of reactants during the synthesis. This stems from the quasi-equilibrium conditions during the chemical conversions. Meanwhile, the principal property of the chiral objects lies, in which they lack a center of symmetry. In addition, it should be noted that among the synthesized products of the

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Miller–Urey experiments analyzed by Bada using the modern liquid chromatography-mass spectrometry method, the highest number of various amino acids was detected in samples obtained in the synthesis system where the electric discharge occurred in an environment with the water steam flowing transverse to the plasma channel [4].

Based on this, dynamic plasma–chemical systems show some promise for use in chiral synthesis. These systems are characterized by an ability to set the specific movement directions of the reactant particles by using either gas dynamics or an electric field. This becomes important after we recall that chirality is a geometric property of the spatial structure of the molecule, that is, it cannot be superposed on its mirror image. In addition, elementary processes are characterized by the proportionality between the process rate and the time during which the reactant particles interact. The advantage of plasma–chemical systems lies in the high rates of the ion–molecular reactions, especially in the case of negative ions with the electron affinity lower than the energy of the chemical bonds, which can easily participate in the synthesis of the organic compounds.

This work is dedicated to the investigation of the optical activity of the products of the organic synthesis in a plasma–liquid system with the rotating gliding discharge [5] submerged in a liquid. The optical activity of the environment is the result of the presence of optical isomers.

The synthesis was conducted in the experimental system with the rotating gliding discharge submerged in liquid [5]. A mixture of ethanol and ammonia was used as the studied liquid. Gas was supplied tangentially to the system axis. CO_2 was used as a working gas. Depending on the direction of the supplied gas flow, the discharge took place in either the clockwise or counterclockwise flow of working gas. The electric field direction in the gas discharge was always perpendicular to the azimuthal component of the gas flow velocity. In addition, the direction of the electric field could be changed by changing the polarity of a discharge power supply.

II. EXPERIMENTAL SETUP AND METHODS

Fig. 1 shows an experimental setup with a rotating gliding discharge submerged in a liquid. The nonequilibrium atmospheric pressure plasma was produced by the rotating gliding discharge [6]–[10], which was successfully used in the plasma-catalytic reforming systems [7]–[9], [11], [12] and plasma-assisted combustion system of hydrocarbons with high viscosity [13]. The plasma generator consists of a central electrode (anode), the upper flange electrode (cathode), and a dielectric chamber with holes for the tangential supply of working gas. The central part of the cathode has a conical shape with a hole in the middle. The diameter of the hole is 3 mm. The rotating gliding discharge is formed between the cathode and anode. The electrodes were made of stainless steel. The distance between the cathode and anode is 1 mm. A quartz tube is placed on top of the cathode and filled with an investigated liquid. The polarity of the electrodes in the system could be changed: when the central electrode is an anode, then the reactor (the part in contact with both the liquid and the flange) electrode is a cathode, and vice versa. The mixture of ethanol and ammonia was used as a studied liquid. Gas was supplied tangentially to the system axis. CO_2 was used as a working gas. The CO_2 flow was 10 L min^{-1}. The gas exit of the system was connected to the cooling setup and the volume for the condensation of the produced gas. Produced gas was directed to the laboratory ventilation and disposed of.

A mixture of ethanol (C_2H_5OH, 96% water solution) and ammonia (NH_4OH, 25% water solution) was treated. The volume of each substance was 50 ml. The mixture was treated for 10 min. The discharge current was approximately 100 mA, and the discharge voltage varied from 1 to 2 kV depending on the polarity of the electrodes (the voltage was 1.5–2 kV when the central electrode worked as the anode and 1–1.3 kV when the central electrode worked as the cathode). The shapes of the oscillograms of the discharge current and voltage (see Fig. 2) were typical for the gliding discharges with the flow that has a velocity component that is transverse to the discharge channel [14]–[16]. They consisted of a constant component and a saw-like signal with a modulation depth of approximately 30%. The voltage was measured using a voltage divider with a 1/480 ratio. The current was measured using a measuring resistor at a nominal 10 Ω. The direction of CO_2 supply was varied: in one case, the gas was supplied

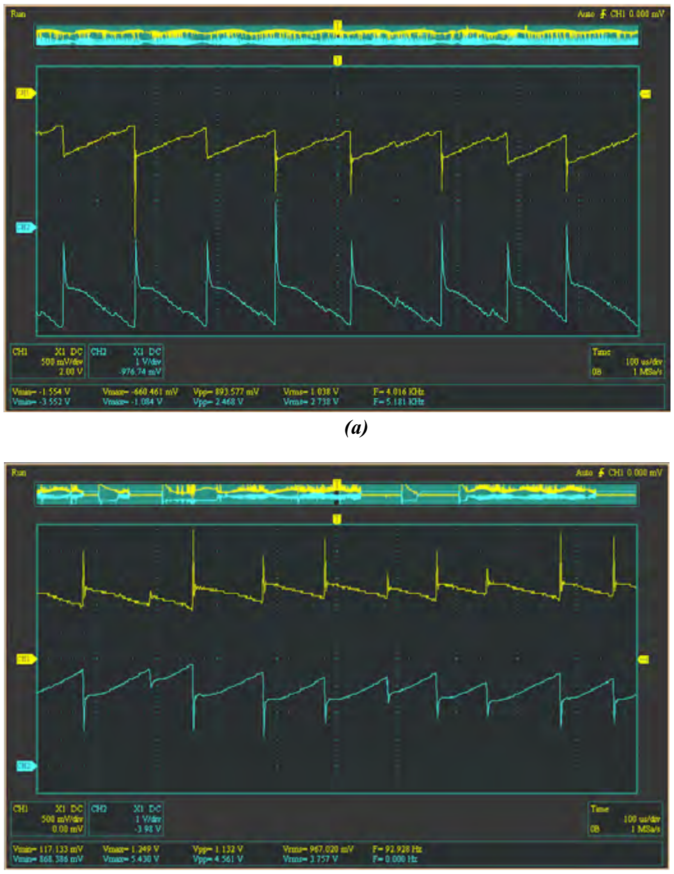

Fig. 2. Oscillograms of currents (CH1 yellow curve) and voltages (CH2 blue curve) in the system with rotating gliding discharge submerged in liquid. Sensitivity of the CH1 = 500 mV/div, sensitivity of the CH2 = 1 V/div, and time = 100 μs/div. (a) Reactor anode. (b) Reactor cathode.

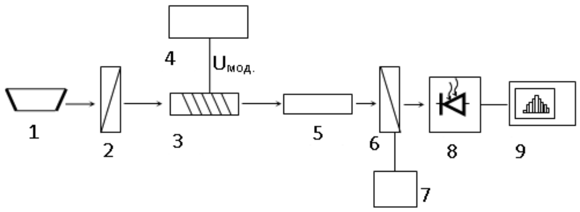

Fig. 3. Scheme of laser modulation polarimeter. (1) Helium–neon laser ($\lambda = 0.63\ \mu$m). (2) Fixed polarizer. (3) Faraday modulator. (4) Modulating U_{mod} generator. (5) Cuvette with the test sample. (6) Analyzer. (7) Vernier scale of reference optical microscope with the dial. (8) Photodetector. (9) Digital spectrum analyzer.

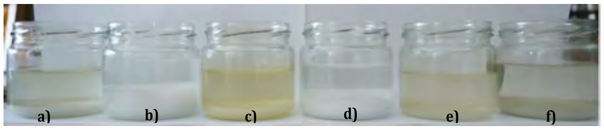

Fig. 4. Photos of solutions taken directly after treatment. (a) Plasma ON-reactor cathode (CO_2 counterclockwise). (b) Plasma OFF (CO_2 counterclockwise). (c) Plasma ON-reactor anode (CO_2 counterclockwise). (d) Plasma OFF(CO_2 clockwise). (e) Plasma ON-reactor anode (CO_2 clockwise). (f) Plasma ON-reactor cathode (CO_2 clockwise).

counterclockwise (if looking at the electrodes from above); in the other case, the gas was supplied clockwise (if looking on the electrodes from above). The volume of the processed mixture was 100 ml. In each system operation mode, five identical solutions were treated, after which they were all mixed in the same vessel.

After the processing, the solutions were analyzed using a polarimeter. A 2-cm cuvette was used. The optical activity of the samples was studied by a laser modulation polarimeter. A scheme of the polarimeter is shown in Fig. 3. The use of a digital spectrum analyzer and a vernier scale of the reference optical microscope with a dial allowed determining the optical activity of the samples with 10-arcsecond precision. The rotation angle of the glucose monohydrate (Glucose-Novofarm 50-mg/ml solution for infusions produced by Novofarm Biosynthesis) was $+26' \ 25'' \pm 10''$, which was obtained by using the cuvette with a 2-mm inner part and a 0.63-μm wavelength of laser radiation.

III. RESULTS AND DISCUSSION

During the treatment of solutions, solids were formed in the system. Those solids changed over time into the liquid phase. This phenomenon occurred both after the plasma treatment of the solution (CO_2 flow with discharge turned on) and after the treatment of the solution with CO_2 without plasma activation (CO_2 flow with discharge turned off). The colors of the solutions did not change over time.

Figs. 4 and 5 show photographs of the solution taken directly after the treatment (see Fig. 4) and two and a half months after the treatment (see Fig. 5).

The solid white phase that formed during the treatment of the solutions in the system may be the urea (carbonic acid diamide, $CO(NH_2)_2$), which forms white crystals that have good solubility in water. Urea is neither acidic nor alkaline [17].

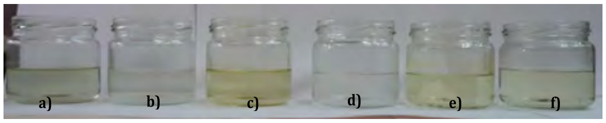

Fig. 5. Photos of solutions taken two and a half months after treatment. (a) Plasma ON-reactor cathode (CO_2 counterclockwise). (b) Plasma OFF (CO_2 counterclockwise). (c) Plasma ON-reactor anode (CO_2 counterclockwise). (d) Plasma OFF(CO_2 clockwise). (e) Plasma ON-reactor anode (CO_2 clockwise). (f) Plasma ON-reactor cathode (CO_2 clockwise).

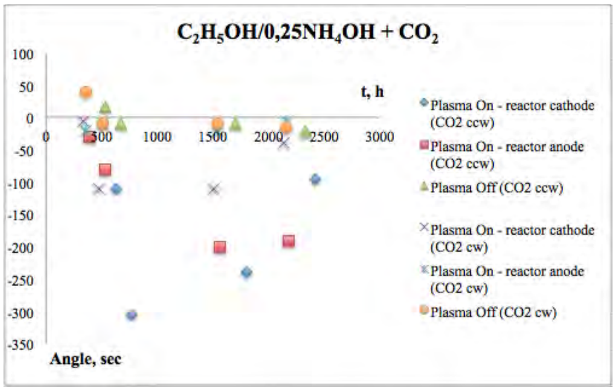

Fig. 6. Optical activity of solutions after treatment in a plasma–liquid system under different modes of operation.

Studies of the optical activity of the treated solutions were conducted on a polarimeter. A cuvette was filled with the solution, and the angle of rotation of the polarization plane of light was measured. For each solution, the time to measure the angle of rotation started from several minutes and could reach up to 20 min. This was caused by the mixing of the solution with the precipitate during the transportation and filling of the cuvette. This led to the scattering of light on the precipitate particles and the change of the polarization angle. After some time, the particles settled, and it was possible to measure the angle of rotation of the polarization plane with an error of ≈10. Fig. 6 shows the dependences of the change in the angle of the rotation of the polarization plane on time after the treatment for different modes of solutions treatment.

The irregularity of the reading over time was observed after the analysis of the treated solutions on the polarimeter. In the case of the system operating modes with the presence of the discharge (for different electrode polarities and flow directions of supplied plasma gas), the measured change of the rotation angle of the light polarization plane significantly exceeds the measurement error but has the same direction for all operating modes. The change of the rotation angle ranges from 10 to 300 arcseconds. The results presented in Fig. 6 point out that, during the operating modes with the presence of plasma, the change of the rotation angle of the light polarization plane is larger when the direction of the flow of the supplied plasma gas is counterclockwise than when it is clockwise. For the modes with different polarities of the electrodes (different directions of the electric field), it is impossible to say with certainty; in that case, the optical activity is higher (the rotation angle of the polarization plane is higher). Further research is needed to answer this question. When the solutions are treated only by the supplied gas in the modes without plasma, the change of the rotation angle of the polarization plane is absent or within the margin of error.

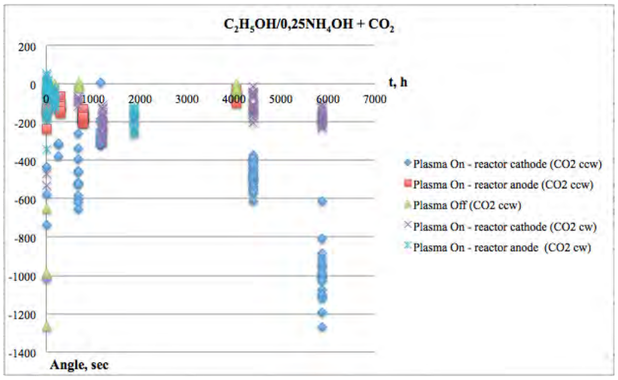

Fig. 7. Optical activity of solutions after treatment in a plasma–liquid system under different modes of operation.

When comparing the obtained results with previous measurements [5] (see Fig. 7), we can observe an almost identical trend.

Previous studies have also shown that the rotation angle of the polarization plane has the greatest significance for the "Plasma ON–reactor cathode" mode when the flow of the supplied gas is directed counterclockwise. Other modes with plasma have almost the same rotation angle. When the solutions are treated only by the supplied gas in the mode without plasma, a large change of the angle is observed on the first day after treatment (20–50 min after treatment). However, on the next day and further, the change of the angle was absent or within the margin of error.

For both studies, the optical activity of the solutions changes up or down for a rather long time after the treatment. This may be caused by chemical transformations, which can still take place in the solutions for a long time. The difference between current and previous studies may be connected to the fact that the activity of previous solutions is measured over a longer time interval.

IV. CONCLUSION

1) The organic synthesis in the dynamic heterophase axially symmetrical system with a significant departure from the equiprobability of the molecule movement direction during the use of reactants without optical activity, such as liquid ethanol (96% C_2H_5OH) and ammonia water (25% NH_4OH), and the gas reactant (CO_2), showed the possibility of the synthesis of the optically active liquid environment.
2) Synthesis without the plasma activation of the gas reactant leads to the products with significant optical activity. However, it is observed only for several hours after the treatment and practically disappears on the next day.
3) Synthesis with the plasma activation of the gas reactant leads to the products with a significant optical activity, which can be still observed for thousands of hours after the treatment. However, the rotation angle of the polarization plane changes over time.
4) In the case of the plasma activation of a gas reactant, the rotation angle of the light polarization plane is significantly influenced by the direction of the rotation of the CO_2 flow. The highest deviation of the rotation angle of the polarization plane takes place when the plasma gas is supplied counterclockwise.

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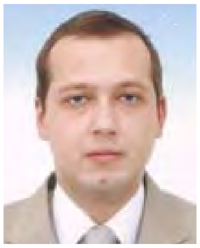

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