

Oxidation of Light Olefines in the Barrier Discharge Reactor

A.N. Ocheredko, S.V. Kudryashov, V.O. Kutenkov*, A.Yu. Ryabov, A.I. Suslov*, and G.S. Shchegoleva

Institute of Petroleum Chemistry SB RAS, 3 Akademicheskoy ave., Tomsk, 634021, Russia, +7(3822) 491-650, +7(3822) 491-457, ks@ipc.tsc.ru

**Institute of High Current Electronics SB RAS, 2/3 Akademicheskoy ave., Tomsk, 634055, Russia*

Abstract – A study of propylene and *i*-butylene oxidation processes in oxygen with octane vapours under the action of dielectric barrier discharge (DBD) plasmas has been performed. It is shown, that the main oxidation products are propylene and *i*-butylene oxides (43.3 and 43.8 wt. %, respectively). Possible reaction pathway for olefines oxidation has been suggested. The experimental results on propylene and *i*-butylene oxidation have shown a principal possibility for production of light olefines oxides under BD conditions without formation of completely oxygenated products and resinous compounds. The suggested reaction pathway indicates that further investigations should be focused expediently on the search of possible ways providing control of the “hot” olefine molecule transformations without undesirable destruction of the carbon skeleton.

1. Introduction

Recently, an increasing interest in practical use of organic synthesis in electrical discharges is observed. However, the developments of new techniques using electrical discharges are constrained by the low reaction selectivity, resins formation and complete destruction of initial organic molecules. Insufficient data on reactions pathways and kinetics of organic compounds transformations in plasmas is another limiting factor.

In our former publication we have shown [1] that production of oxygenated hydrocarbons of various classes is possible in the barrier discharge without formation of resins and completely oxygenated compounds. Those results were achieved due to an efficient removal of reaction products from the discharge area by the liquid hydrocarbon film formed in the course of supersaturated hydrocarbon vapour condensation at the cold reactor walls. So, the oxidation of hexane, cyclohexane and cumol mainly leads to formation of hydroxyl and carbonyl compounds - alcohols, aldehydes and ketones having the same number of carbon atoms as the initial compound. The main product of cyclohexene oxidation is epoxy-cyclohexane ~ 62 wt. %.

It was shown in the paper [2] the principal possibility of the selectivity control for reaction of cyclo-

hexene oxidation. Maximal yield of cyclohexene oxide was ~ 72 wt. %. However, the most interest for petrochemical synthesis represent oxidation products of light olefines.

In this paper the results on oxidative conversion of propylene and *i*-butylene in the barrier discharge reactor are presented.

2. Experimental

Oxidation of propylene and *i*-butylene was carried out in the presence of octane vapour in order to obtain a liquid hydrocarbon film on the reactor walls, which dissolves main part of reaction product, and hence, removes them from the discharge area. In our earlier study on oxidation of heavy alkane molecules, we have shown, that their vapours sufficiently effect only the high energetic part of the electron energy distribution function in the gas discharge plasmas, which lies much higher than the energy threshold for dissociation of oxygen molecule by electron impact. So, the presence of octane vapour doesn't effect considerably on initiation of the oxidation process by the oxygen atoms O. This result was confirmed both by numerical simulations and experimental measurements. In the present work a flowing type BD reactor of coaxial design was used for study of the light olefines oxidation process.

General view of the experimental setup with BD reactor is given in the figure 1. In the experiments a glass BD reactor (8) was used with two dielectric barriers. Dielectric barriers were formed by two pyrex glass tubes of 2 mm in thickness and 120 mm in length, separated by the gas discharge gap of 1.1 mm. The outer tube had an outer diameter of 32 mm and was covered by the aluminium foil serving as a ground electrode. To provide application of high voltage potential on the surface of another dielectric barrier the inner tube was filled by 5% sodium aqueous solution. The temperatures of evaporator (5) and reactor walls were maintained at 120 °C and 20 °C, respectively. Supersaturated octane vapour was created in the evaporator and then mixed with oxygen and olefine in the mixing cell (4). Thus prepared gaseous mix was passed through the discharge gap, where octane condensation occurred at the cooled reactor walls. The residence time of atmospheric pressure gaseous mix inside discharge space was of 10.5 s.

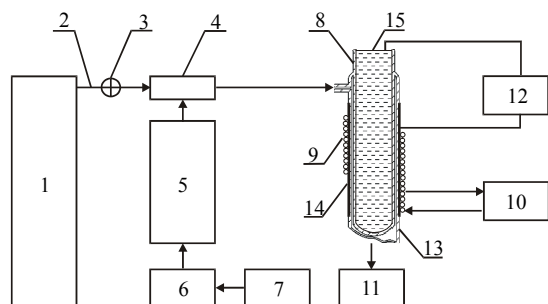


Fig. 1. Schematic representation of the reaction system. 1 - oxygen tank with a standard pressure regulator; 2 - gas line; 3 - needle valve; 4 - mixing cell; 5 - evaporator; 6 - peristaltic pump; 7 - hydrocarbon container; 8 - reactor; 9 - heat exchanger; 10 - thermostat; 11 - receiver; 12 - high voltage generator; 13 - dielectric barrier; 14 - ground electrode; 15 - high voltage electrode (5% NaCl aqueous solution)

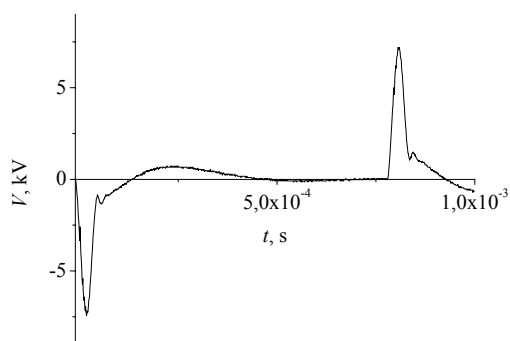


Fig. 2. Voltage waveforms at the electrodes of BD cell

Discharge feeding was provided by high voltage repetitive-pulsed generator (12), having voltage pulses with an amplitude up to 20 kV, a pulse duration of 40 μ and a repetition rate of 1.5 kHz. Recording of the voltage and current waveforms as well as amount of electrical charges transferred through BD cell was implemented using two-channel oscilloscope ACK 3106. The estimated error of current, voltage and charge measurements did not exceed 10%. In the figure 2 are presented voltage waveforms at the electrodes of BD cell. After application of this voltage to the electrode system a uniform glow discharge was formed between dielectric barriers (figure 3(b)). The non-filamentary glow discharge was used here to increase the power efficiency of BD reactor [3]. For comparison in the figures 3(a) and 3(b) are presented the side views for two different BD discharge regimes corresponding to a filamentary and glow-type discharges. It can be seen that transition to the glow mode is achieved when the pulse duration is decreased from 1 ms to 40 μ s.

The active component of the power P dissipated in the gas discharge was measured using voltage-charge characteristic technique. Typical view of Lissajous figure for our flowing type reactor is given in

the figure 4. The energy deposited into discharge W for one period of the voltage action was determined by direct integrating of the instant charge q transferred through BD cell:

$$W = \int q dV, \quad P = fW, \quad (1)$$

where V is the voltage across the electrode system. In the experiments the active component of the power was from 1 to 5 W.

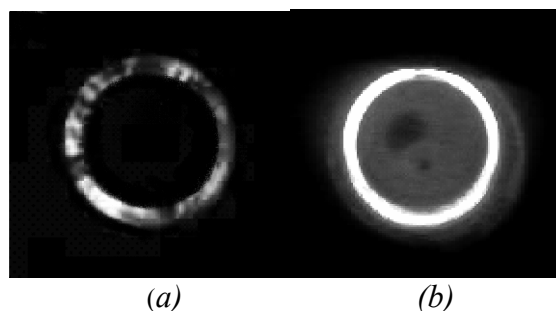


Fig. 3. Side view of BD after application of the repetitive pulsed voltage of two various forms to the electrode system of BD: with a pulse duration of 1 ms (a) and 40 μ s (b). (a) – the gas discharge with a non-uniform current distribution; (b) glow-type discharge

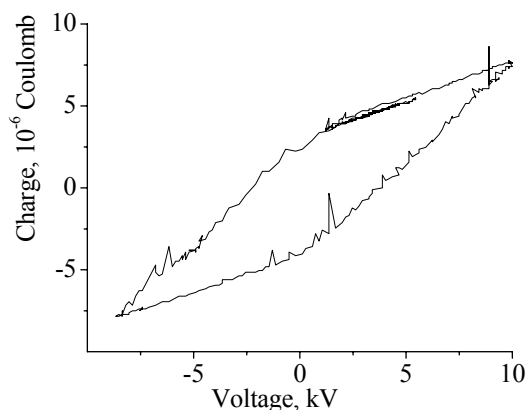


Fig. 4. Voltage-charge characteristic of the flowing type BD reactor

The analysis of gaseous and liquid products was performed using gas-liquid chromatography and chromat-mass-spectrometry technique (gas chromatograph Unicam-610, FID, – U.K. and gas chromatograph/mass-spectrometer NERMAG/R10-10/C – France). The errors in determination of product concentrations for analyzed mixtures did not exceed 5%.

The following data characterizing considered process were used as initial values of experimental parameters: the volume flow rate through the reactor for oxygen, olefine and octane were, respectively, of 3.0, 0.6 and 6 \cdot 10⁻³ l/h; the specific energy deposited into discharge was of 1 kW \cdot h/l.

Table 1. The conversion value, the oxidation products and the selectivity of their formation for propylene and *i*-butylene*.

Olefine	X, wt. %	Oxidation products	Selectivity, wt. %
Propylene	1.56	Propylene oxide	43.3
		Acetone	30.9
		Acetaldehyde	10.2
		Methanol	3.4
		Water + formaldehyde	12.2
<i>i</i> -butylene	6.74	<i>i</i> -butylene oxide	43.8
		2-methylpropanal	23.9
		Acetone	19.2
		Methanol	4.6
		Water + formaldehyde	8.5

*The conversion value has been obtained for one pass of the gas mix through the reactor whereas the residence time was ~ 10.5 s.

3. Results and discussion

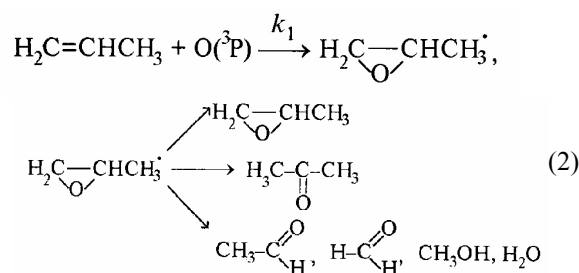
The conversion values and the compositions of the output products for propylene and *i*-butylene are presented in the table 1. It is seen from the Table 1, that the main reaction products are the respective olefines oxides. In the course of the oxidative conversion of propylene and *i*-butylene the destruction of olefine molecule takes place in comparison to the reaction of cyclohexene oxidation. At the same time, there were not found CO, CO₂, acids and resinous compounds, what is characteristic in principle for current results in comparison to those ones presented in the earlier publications on oxidation of light olefines in the electrical discharges [4-6].

It should be noticed, that octane conversion also takes place. For data presented in table 1 the octane conversion in both cases was ~ 0.5 wt.%. As a result, hydroxyl and carbonyl compounds are formed, which are characteristic for octane oxidation products [7].

In the work [2] the possible reaction pathway for cyclohexene oxidation has been suggested, where formation of reaction products can occur by two different routes. In the first case cyclohexene oxide, cyclohexanone, cyclopentylmethanal are formed, and in the second one - cyclohexanone, cyclohexanol and bicyclohexenyl.

Since unsaturated oxygenated compounds weren't found in the composition of the oxidation products, one can suggest that main reaction pathway occurs according to the first direction, which involves activation of the oxygen molecule by electron impact. An explanation for this behaviour can be higher dissociation energies for propylene and *i*-butylene by electron impact in comparison to those ones for oxygen and cyclohexene [8].

Using suggested reaction pathway for cyclohexene oxidation one can describe in a similar way the possible oxidation mechanism for propylene by the following kinetic scheme:



Here, acetaldehyde, formaldehyde, methanol and water formation occurred as a result of the destruction of the "hot" propylene oxide molecule followed by radical reactions of fragments formed after its decomposition. In case of cyclohexene oxidation [1,2] the "hot" olefine oxide molecule doesn't undergo decomposition process.

Using simple calculations one can verify the validity of suggested oxidation mechanism for propylene and *i*-butylene. For reaction of olefine oxidation in the reactor operating in a steady-state flowing mode the following simple expression is valid:

$$\frac{w_1}{w_2} = \frac{X_1}{X_2}, \quad (3)$$

where w_1 , w_2 , X_1 , X_2 are the oxidation rates and conversions for propylene and *i*-butylene, respectively.

Starting from suggested reaction pathway one can write an expression for the oxidation rate w_1 of propylene:

$$w_1 = \frac{d[\text{C}_3\text{H}_6]}{d\tau} = k_1[\text{O}({}^3\text{P})][\text{C}_3\text{H}_6], \quad (4)$$

Similar relation is also valid for the rate w_2 .

When the discharge power is maintained at a constant value and other experimental parameters are also identical, then the rates of atomic oxygen production

for the gas mixes with propylene and *i*-butylene are also about a constant value, because their molecules have rather close values of electron scattering cross-sections in the gas discharge. Hence, one can write the expression (3) in the following manner:

$$\frac{k'_1}{k'_2} = \frac{X_1}{X_2}, \quad (5)$$

where k'_1 and k'_2 are the rate constants for atomic oxygen interactions with propylene and *i*-butylene, respectively. Using known data for k'_1 and k'_2 and the measured values for X_1 and X_2 from table 1, we will obtain:

$$\frac{k'_1}{k'_2} = \frac{2.2 \cdot 10^{12} \text{ см} \cdot \text{моль}^{-1} \cdot \text{с}^{-1}}{1.2 \cdot 10^{13} \text{ см} \cdot \text{моль}^{-1} \cdot \text{с}^{-1}} = 0.183, \quad (6)$$

$$\frac{X_1}{X_2} = \frac{1.56}{6.74} = 0.231. \quad (7)$$

It is seen, that a satisfactory agreement is observed between relations (6) and (7) calculated from the rate constants data and using measured conversion values from table 1. The deviation for relations (6) and (7) is ~ 20 %.

4. Conclusions.

It is shown a principal possibility of the light olefines oxides production in the atmospheric pressure BD

reactor without formation of resinous and completely oxygenated products. The reaction pathway for oxidation of light olefins in oxygen under conditions of an efficient removal of the reaction products from the discharge area has been suggested.

5. References.

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