

Applications of the Barrier Glow Discharge for Conversion of C₁-C₈ Hydrocarbons

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Abstract – It is shown, that the barrier discharge (BD) can be efficiently applied to conversion of alkanes with the number of carbon atoms greater than 4.

The experiments were carried out in the flowing type BD reactor, where the possibility for an efficient removal of the end product from the discharge area has been provided.

This installation setup allows the study of the basic reaction pathways for C₁-C₈ oxidative conversion (in oxygen) at atmospheric gas pressure and the ambient gas temperature (20 °C). The process of isomer formation from *n*-hexane and cyclohexane in helium was also studied using this installation. The pulsed-power supply was used for the plasma chemical reactor feeding, which provided the following performances: the voltage amplitude was up to 20 kV; the repetition rate of bipolar voltage pulses from 1 to 3 kHz; the pulse duration of 40 μs. This operating mode allowed one to obtain a minimal specific energy consumptions for oxygenated compounds synthesis ~ 5 kW·h/kg. It has been shown, that oxidation of C₁-C₈ hydrocarbons (HC) including cyclohexane follows the general gas phase mechanism of HC oxidation with a short chain (4 parts). Energy consumptions for isomer production are by nearly one order of magnitude higher as compared to C₅-C₈ oxidation because of the non-chain reaction route for product formation.

1. Introduction

Common methods of natural gas conversion into valuable products imply creation of high pressure and high temperature conditions in catalyst-based reactors. Therefore, much attention is paid recently to alternative techniques for HC conversion [1]. In the last few years some authors suggest to use the plasma chemical reactors for air purification from the volatile organic compounds [2] and for organic synthesis [3]. The main factors restricting the practical application of plasma chemical technologies are low selectivity of plasma chemical processes and high energy expenses for production of desirable compounds. Besides, the absence of reliable information on the kinetic

processes, mechanisms of organic compound transformations in the electric discharges, constrain the implementation of these processes in practice. In this paper the processes of oxidative conversion of C₁-C₈ and production of HC with isomer structure in inert gases has been considered under conditions of an efficient removal of reaction products from the discharge area. The experiments were carried out in a flowing type DBD reactor at atmospheric gas pressure and the ambient temperature (20 °C).

2. Experimental

Installation setup used for experiments is described in more details in the paper by S.V. Kudryashov, et al. "Oxidation of light olefines in the barrier discharge reactor" of current proceedings. Dielectric barriers of BD cell were formed by two coaxial glass tubes separated by 1.1 mm gas discharge gap. The supersaturated hydrocarbon-vapour from evaporator was mixed with a carrier gas in a mixing cell and passed then through the discharge gap. In experiments the efficient removal of the end products from the discharge area was provided by a flowing down liquid hydrocarbon film formed in the course of HC vapor condensation on the cold reactor walls. The gas flow rate of feed gas through the reactor was 3.6 l·h⁻¹. The residence time of the gas-vapour mixture in the discharge area was of 10.5 s. The analysis of the liquid reaction products was carried out using gas chromatography (a Unicam-610 chromatograph, FID, UK) and chromatomass-spectrometry (NERMAG/R10-10/C chromatomass-spectrometer, France) techniques.

For the plasma chemical reactor feeding, the repetitive pulsed-power supply was used, which provides the following performances: the voltage amplitude was up to 20 kV; the repetition rate of bipolar voltage pulses from 1 to 3 kHz; the pulse duration of 40 μs. Repetitive-pulsed high voltage generator was applied to realize glow type BD in the plasma chemical reactor. The active power dissipated in the gas discharge was measured using voltage-charge characteristic technique.

Electrical parameters measurements, such as voltage and current waveforms, as well as amount of electrical charges transferred through BD cell were

performed using two-channel oscilloscope ACK 3106. The estimated error of current, voltage and charge measurements did not exceed 10%.

3. Oxidation of C₁-C₈ hydrocarbons

Table 1. Compositions of HC oxidation products.

Hydro-carbon	Oxidation products	Wt. %
Pentane	Mix: Pentanal, 3-,2-	58.62
	Pentanone	13.42
	3-Pentanol	24.62
	2-Pentanol	3.02
	1-Pentanol	0.32
	Other	
Hexane	Hexanal	22.06
	Mix: 3-,2- Hexanone	21.45
	3-Hexanol	27.49
	2-Hexanol	19.90
	1-Hexanol	7.74
	Other	1.34
Heptane	Heptanal	9.75
	Mix: 4-, 3- Heptanone	18.20
	2-Heptanone	18.52
	4-Heptanol	10.57
	3-Heptanol	18.60
	2-Heptanol	15.90
	1-Heptanol	5.97
	Other	2.46
Octane	Octanal	17.43
	Mix: 4-, 3-Octanone	17.49
	2-Octanone	16.13
	4-Octanol	14.68
	3-Octanol	13.65
	2-Octanol	12.96
	1-Octanol	4.12
	Other	3.53
Cyclo-hexane	Cyclohexanol	49.44
	Cyclohexanone	40.78
	Water	9.52
	Other	0.23
Methane	Ethylene	11,7
	Ethane	7,1
	Water + formaldehyde	16,9
	Methanol	19,5
	Dimethyl ether	10,6
	Methylformiat	16,1
	Formic acid	4,5
	Other	13,6

The composition of HC oxidation products in a flow type reactor are shown in Table 1. As is seen from the Table 1, HC oxidation occurs with a high selectivity and leads mainly to the formation of alcohols and carbonyl compounds - aldehydes and ketones. Resinous compounds, acids and hydroperoxides normally formed at the auto-oxidation are absent in

the composition of the reaction products. A high selectivity that is not characteristic for most plasma chemical processes evidence that the HC film flowing down the reactor walls efficiently withdraws the reaction products from the discharge area thus preventing their further conversion and resinification. The present experimental data also indicate a common oxidation mechanism of all HC.

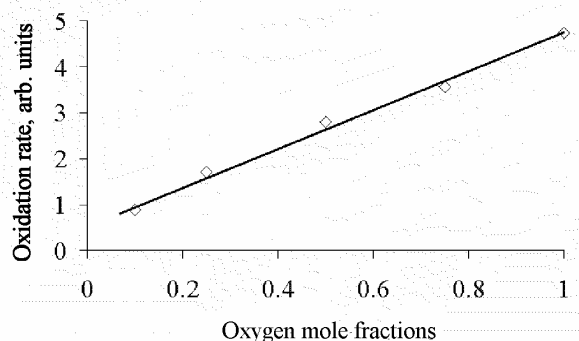
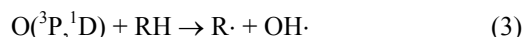
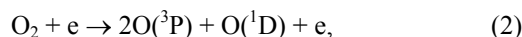


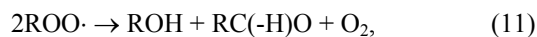
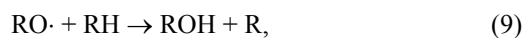
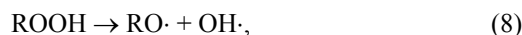
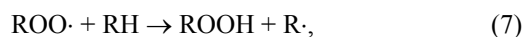
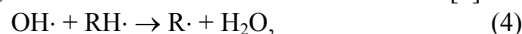
Fig. 1. Oxidation rate of cyclohexane versus oxygen mole concentration.

In the present paper numerical simulation of cyclohexane oxidation in the barrier discharge reactor has been performed. Numerical simulation of DBD has shown that initiation stage of the chain reaction of HC oxidation in the barrier discharge can be described by the following reactions:



This result coincides with the experimentally measured dependence of the oxidation rate versus oxygen mole concentration in the HC-oxygen mix presented in the Fig.1. It is seen from the Fig.1 that this dependence features a linear character. Variation of oxygen concentration was realized in experiments using oxygen-helium mix as a feed gas with different oxygen concentrations.

The further progress of the chain reaction, probably, follows the classic oxidation mechanism [4]:



where ROH and RC(-H)O are hydroxyl and carbonyl components, respectively.

The thermodynamic analysis of the reactions (4-11) at given experimental conditions has shown that the reaction of the disproportionation of peroxide radicals (11) is the main pathway for formation of alcohols and carbonyl compounds.

To validate the suggested mechanism, kinetic calculations of cyclohexane oxidation in BD have been performed. According to numerical calculations the mechanism of cyclohexane oxidation in the barrier discharge is represented mainly by the processes of the chain rupture (5, 10-11). A leading role is played by the reaction of disproportionation of cyclohexylperoxide radicals [4] that leads to formation of cyclohexanol and cyclohexanone. As the continuation of chain occurs mainly by reactions (3, 4, 6), it is possible to suggest that the chain reaction of cyclohexane oxidation is characterized by a short chain, at the absence of branching out stages. Characteristic times of formation of the final products are $\sim 10^{-3}$ s for cyclohexanol and cyclohexanone and $\sim 10^{-5}$ s for water, hydrogen peroxide and bicyclohexyl.

The composition of theoretically obtained reaction products is summarized in Table 2.

Table 2. The composition of cyclohexane oxidation products (simulation results)

Component	Wt %
Cyclohexanol	46.38
Cyclohexanone	42.79
Water	8.08
Hydrogen peroxide	0.18
Bicyclohexyl	2.57

As to methane, then in this case the gaseous and volatile organic compounds (e.g., formaldehyde and methanol) are formed in BD reactor, which are exposed by the secondary action of gas discharge plasmas. As a result, a great amount of secondary conversion products are formed inside the reactor: dimethyl ether, methylformiat and ethylene. It leads to the low process selectivity and to increase of the energy consumptions for valuable oxygenated compound production. Nevertheless, a relatively small concentration of the formic acid, the absence of carbon monoxide and carbon dioxide in reaction products indicate that no deep methane oxidation occurs in the reactor. In the experiment on partial oxidation of methane the initial gas mix composition consisted of methane (94%) and oxygen (6%). The initiation of the oxidation process in this mix starts mainly with formation of CH_3^\bullet , while peroxide radicals $\text{CH}_3\text{OO}^\bullet$ occur just after attachment of molecular oxygen to CH_3^\bullet . So, the number of parts in the reaction chain in this case decreases to 1 as compared to cyclohexane oxidation process in oxygen, when initiation starts by oxygen atoms. It is just

the second important reason for increased energy consumptions occurred for methane oxidative conversion in BD.

The optimal conditions for $\text{C}_5\text{-C}_8$ oxidation with energy consumptions for the end product synthesis of 5 kW·h/kg were obtained in an uniform glow type BD discharge, while the total selectivity of oxygenated HC formation was of $\sim 90\%$. It is of interest for various applications in chemical industry, e.g. for adipic acid production. The glow type BD is also favourable for reactor optimization due to wide range of the operating electric parameters, such as discharge current and voltage amplitude, and to the uniform current distribution on the dielectric surface. The discharge power in the above experiments was from 1 to 5 W.

4. Production of isomer hydrocarbons

Hydrocarbon transformations initiated by electric discharges in inert gases are of interest for production of HC with isomer structure, which are valuable components for the motor fuels.

We have shown in the previous section that under conditions of an efficient withdrawn of reaction products from the discharge area the oxidation of some HC is possible with a high selectivity. The results obtained under the action of BD discharge on cyclohexane and *n*-hexane in the mixtures with helium representing another technique for HC conversion. The compositions of HC conversion products in helium are shown in Table 3. The experiments were carried out using the same installation setup as described in the paper by S.V. Kudryashov, et al. "Oxidation of light olefines in the barrier discharge reactor" of current proceedings.

Table 3. The compositions of cyclohexane and *n*-hexane conversion products in helium.

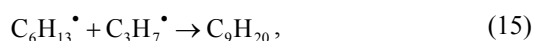
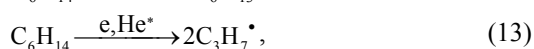
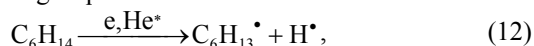
Hydrocarbon	Products	Wt. %
Cyclohexane	Dimethylcyclopentane	1.48
	Propenylcyclohexane	12.85
	Methylpropenylcyclohexane	8.06
	Methylpropylcyclohexane	10.54
	Butenylcyclohexane	4.94
	Hexenylcyclohexane	10.20
	Cyclohexenylcyclohexane	6.58
	Bicyclohexyl	45.30
Hexane	<i>i</i> -octanes	1.62
	<i>i</i> -nonanes	17.86
	<i>i</i> -decanes	8.03
	<i>n</i> -decane	2.43
	<i>i</i> -dodecane	65.97
	<i>n</i> -dodecane	4.06

It is seen from the Table 3, that under the action of BD plasmas on hexane vapour in helium, branched hydrocarbons $\text{C}_8\text{-C}_{12}$ (93.48 wt. %) occur, and in case

of cyclohexane – bicyclohexyl, alkyl- and alkenylsubstituted cyclohexanes. There were no higher compounds in the composition of reaction products and no resinification processes were observed inside the reactor. Much lower values of HC conversion rates (by the order of magnitude) occurred in the experiments with helium in comparison to those ones with the oxygen mixtures, are caused by the difference between the energy thresholds for electron impact dissociation of oxygen (~ 6.2 eV) and HC (> 8 eV) [5-7]. The mean electron energy in the barrier discharge plasma is of ~ 2-3 eV.

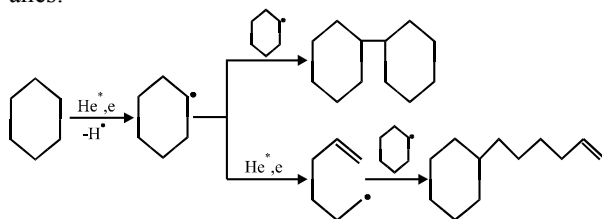
The most possible route for formation of *n*-hexane conversion products is recombination of HC radicals formed under the action of gas discharge. The composition of the final products allows suggestion that under experimental conditions the main radicals are hydrogen atom and hexyl radical. Occurrence of C₈-C₁₀ hydrocarbons indicates that C-C bonds break of hexane molecule takes place with formation of radicals having the number of carbon atoms less than initial molecule had. Considerable portion of nonanes shows that propyl radicals dominate in discharge as a result of C-C bonds break.

Starting from the above considerations one can describe formation of C₉ and C₁₂ hydrocarbons by the following sequence of reactions:



where He* are the meta-stable helium atoms.

As to cyclohexane transformations, the composition of compounds obtained in BD shows that dimer formation from initial molecules in this case also play a principal role. Main distinction is connected with the features of C-C bond break by electron impact, which results in occurrence of alkenylsubstituted cyclohexanes:



Other groups (methyl, methylene) can arise both from the splinters of cyclohexane, and from its decomposition products.

Specific energy consumptions for isomer production in BD turns out to be rather high – more than 50 kW·h/kg. The process has non-chain character and for

its efficiency enhancement special studies of other types of discharges are required, where it is possible realization of the chain reaction pathway for isomer production.

5. Conclusions

The results obtained have convincingly proved that it is possible to synthesize valuable organic compounds (e.g. cyclohexanol and cyclohexanone) in the barrier discharge plasma under specific conditions, which allow an efficient removal of the reaction products from discharge area with considerably high selectivity and efficiency.

The conversion of cyclohexane and *n*-hexane for the barrier discharge conditions in He has been studied. The BD action on *n*-hexane vapors leads to formation of branched HC (93.48 % wt.). The main products of cyclohexane conversion are bicyclohexyl (45.3), alkyl- and alkenylsubstituted cyclohexanes (48.12 % wt.).

The results obtained for *n*-C₁-C₈ and cyclohexane oxidation, and on their transformations in inert gases can be a basis for development of new methods for fossil fuels utilization. Oxidation products C₅₊ (alcohols and carbonyl compounds) and isomers are of practical importance, in particular for use as a raw material for production of caprolactam, polyamide fibers and polyamide resins, and also as components for the motor fuels for enhancement their octane number.

6. References

- [1] H. Suhr, Plasma Chem. Plasma Process. **9** 7 (1989)
- [2] W.C. McCulla, L.A. Rosocha, W.C. Neely et. all, in *Proc. First INEL Plasma Applications to Waste Treatment Workshop*, 1991, 13 p.
- [3] T. Kishida, N. Yamada, T. Nozaki, K. Okazaki, Thermal Science and Engineering, **7**, 1 (1999).
- [4] N.M. Emanuel', E.T. Denisov and Z.K. Maizus, *Chain Oxidation Reactions of Hydrocarbons in Liquid Phase*, Moscow, Nauka, 1965, 329 p. (in Russian).
- [5] Samoilovich V.G., Gibalov V.I., Kozlov K.V., *Physical Chemistry of the Barrier Discharge*, Moscow, Moscow State University Publishers, 1989, 175 p. (in Russian).
- [6] Slovetskiy D.N., *Khimiya plazmy*, Moscow, Energoatomizdat, 1981, P. 189-229 (in Russian).
- [7] Yeregin E.N. *Elements of Gas Electrochemistry*, Moscow, Moscow State University Publishers, 1968. - 211 p. (in Russian).