ISSN 0965-5441, Petroleum Chemistry, 2012, Vol. 52, No. 1, pp. 60–64. © Pleiades Publishing, Ltd., 2012.
Original Russian Text © S.V. Kudryashov, S.A. Perevezentsev, A.Yu. Ryabov, G.S. Shchegoleva, E.E. Sirotkin, 2012, published in Neftekhimiya, 2012, Vol. 52, No. 1, pp. 66–70.

Study of the Products of Benzene Transformation in the Presence of Argon, Hydrogen, and Propane–Butane Mixture in Barrier Discharge

S. V. Kudryashov, S. A. Perevezentsev, A. Yu. Ryabov, G. S. Shchegoleva, and E. E. Sirotkin
Institute of Petroleum Chemistry, Siberian Branch, Russian Academy of Sciences, Tomsk, Russia
e-mail: ks@ipc.tsc.ru

Received March 27, 2011

Abstract—The conversion of benzene in a medium of Ar, H_2, and propane–butane mixture in a dielectric-barrier discharge reactor, accompanied by polymerization yielding liquid and solid compounds, has been investigated. The amount of polymerization products reaches 79.7 wt %. Addition of H_2 to benzene reduces the amount of benzene-soluble polymer-like compounds in the products to ~61 wt % and precludes the formation of solid polymerization products. The transformation of benzene with a propane–butane mixture yields alkylbenzenes (up to 38.5 wt %) and liquid alkanes (to 20.5 wt %, mainly with a branched structure). It has been found that an increase in benzene flow rate from 0.08 to 0.4 cm^3/min in the case of benzene conversion with the propane–butane mixture can significantly reduce the amount of polymerization products from 56.7 to 9.1 wt %.

DOI: 10.1134/S0965544112010057

Studies devoted to reactions of aromatic compounds in electric discharges are much less in number than those on the transformations of alkanes. Recent publications mostly concern processes for post-treatment of industrial emissions for removal of aromatic compounds (benzene, toluene, xylenes, etc.), which either undergo deep oxidation to CO, CO_2, and H_2O or polymerize under discharge conditions [1, 2]. Investigations of benzene transformation in electric discharges of various types [3, 4] revealed as main products biphenyl and phenylcyclohexadienes in small quantities and polymerization products making up to 80% of the total product mass.

We attempted to eliminate the unwanted process of polymerization of aromatic compounds, taking benzene transformation in dielectric-barrier discharge (DBD) plasma as an example, by selecting different reaction conditions, including admixture of compounds intended for advanced use, such as the propane–butane fraction (PBF) of natural or associated gas, to manufacture valuable chemical feedstock (alkylbenzenes, branched-chain hydrocarbons).

In this paper, we report the results of experimental study of the transformations of benzene in an Ar, H_2, and propane–butane medium in a DBD reactor.

EXPERIMENTAL

One of the reasons for low selectivity of plasma-chemical reactions is the lack of an effective channel for product withdrawal from the discharge zone. Previously, we proposed to use a liquid hydrocarbon film running down the reactor walls for the removal of reaction products from the discharge zone [5]. In this study, benzene was used as a hydrocarbon to form the liquid film on the reactor walls. The experimental setup is sketched in Fig. 1.

A gas stream from cylinder *1* by pipeline *2* through fine-tuning valve *3* is directed to mixer *4*, in which it is mixed with benzene vapor. Benzene is vaporized in evaporator *5* consisting of metal capillary *6* and tubular furnace *7*. Benzene is fed into the evaporator by peristaltic pump *8* from tank *9*. The evaporator temperature of 120°C is monitored with chromel–alumel thermocouple *10* connected to digital millivoltmeter *11*. From the mixer, the vapor–gas mixture is directed into plasma reactor *12*. The gas-discharge flow reactor is made of Pyrex glass and has the 10-cm long working area and the volume of 12.3 cm^3. The electrode system consists of grounded outer electrode *13* and coaxial high-voltage inner electrode *14*. Discharge gap *15* between the dielectric barriers is 1 mm, and the dielectric-barrier thickness is 2 mm. Benzene vapor condenses at the reactor walls cooled to −10°C. Further, the benzene concentration in the vapor–gas mixture is established on the level of ~6 vol %. The resulting condensate containing dissolved reaction products flowed as a film down to collector ~6 equipped with a reflux condenser. The reactor walls were temperature-controlled with coil *17* connected with thermostat *18*. Discharge was excited with high-voltage pulses supplied from generator *19*. The pulse voltage and discharge parameters were recorded by Aktakom ASK 3106 two-channel digital oscilloscope *20* with a band-

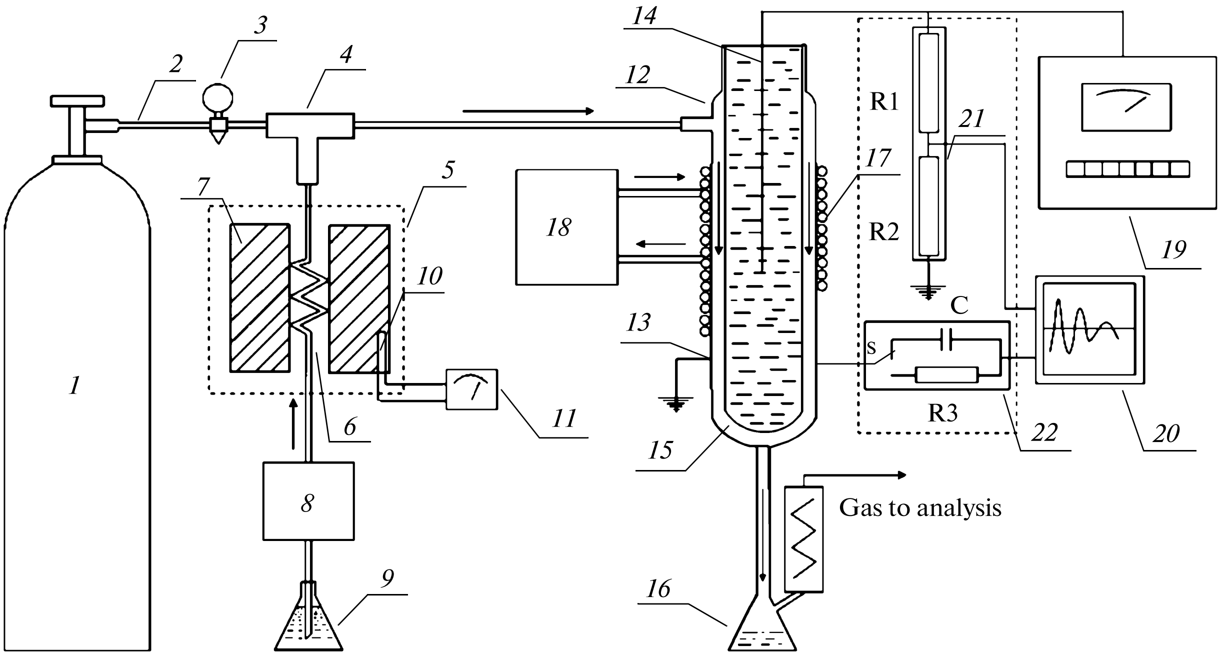

Fig. 1. Schematics of the experimental setup and measurement of discharge parameters:
(*1*) gas cylinder, (*2*) pipeline, (*3*) gas fine-tuning valve, (*4*) mixer, (*5*) evaporator, (*6*) metal capillary, (*7*) tubular furnace, (*8*) peristaltic pump, (*9*) tank with benzene, (*10*) chromel–alumel thermocouple, (*11*) digital millivoltmeter, (*12*) plasma reactor, (*13*) grounded electrode, (*14*) high-voltage electrode immersed in a saturated NaCl solution, (*15*) discharge gap, (*16*) collector with a reflux condenser, (*17*) cooling coil, (*18*) thermostat, (*19*) generator of high voltage pulses, (*20*) digital oscilloscope, (*21*) voltage divider ($R_1 = 1$ MΩ, $R_2 = 1$ kΩ), and (*22*) capacitance ($C = 500$ pF) and current ($R_3 = 5.2$ Ω shunts); s is the switch.

width of 100 MHz. The schematic circuit diagram of recording the discharge parameters is shown in Fig. 1. Figure 2 depicts pulsed voltage and current oscilloscope traces and the charge–voltage characteristic of the discharge.

The active discharge power W (W) was calculated by the equation:

$$W = fV_iq \quad (1)$$

where f is the voltage pulse repetition frequency (2 kHz), V_i is the discharge operation voltage, and q is the charge transferred per pulse. The value of q was determined from the charge–voltage curve [6]. The procedure is graphically illustrated in Fig. 2b. The active discharge power was 21.6 W. The gas (Ar, H_2, PBM) flow rate was constant, 15 cm^3/min, in all experiments. The flow rate of benzene was varied within 0.08–1 cm^3/min.

The reaction products were identified and determined by GLC and GC–MS (gas chromatography–mass spectrometry). The chromatographic analysis of the liquid products was performed on a chromatograph with a flame-ionization detector in the temperature programming mode: isothermal holding at a column temperature of 70°C for 10 min followed by heating to 180°C at a heating rate of 5°C/min, on a capillary column ($l = 100$ m, $d_{\text{in}} = 0.25$ mm) coated with the OV-101 liquid stationary phase using helium as the carrier gas. Mass spectra were obtained on a Shimadzu QP 5050 A GC–MS instrument using a capillary column with the DB–5 liquid stationary phase ($l = 30$ m, $d_{\text{in}} = 0.25$ mm).

The gaseous reaction products were determined in the isothermal mode on the chromatograph with a thermal conductivity detector. Packed columns with molecular sieves 5A ($L = 2$ m, $d_{\text{in}} = 3$ mm, $T_{\text{col}} = 30$°C) and Porapak QS 80/100 mesh ($L = 3$ m, $d_{\text{in}} = 3$ mm, $T_{\text{col}} = 100$°C) as sorbents were used.

Benzene-soluble polymer-like compounds (SPC) formed by the reaction were isolated by evaporation of volatile products in an argon stream. Insoluble polymer-like compounds (IPC) were removed mechanically from the reactor walls. The molecular mass of SPC was determined cryoscopically in naphthalene according to the procedure given in [7]. The SPC were investigated by IR (Nicolet 5700 FTIR spectrometer) and NMR (Avance AV 300 Fourier-transform NMR spectrometer) spectroscopy.

RESULTS AND DISCUSSION

Table 1 shows the product composition for the transformation of the C_6H_6/Ar mixture in the DBD reactor at different benzene flow rates. The main products are SPC, IPC, biphenyl, and phenylcyclohexadienes (phenylcyclohexa-1,3-diene and phenylcyclohexa-1,4-diene). Monoalkylbenzenes, cyclo-

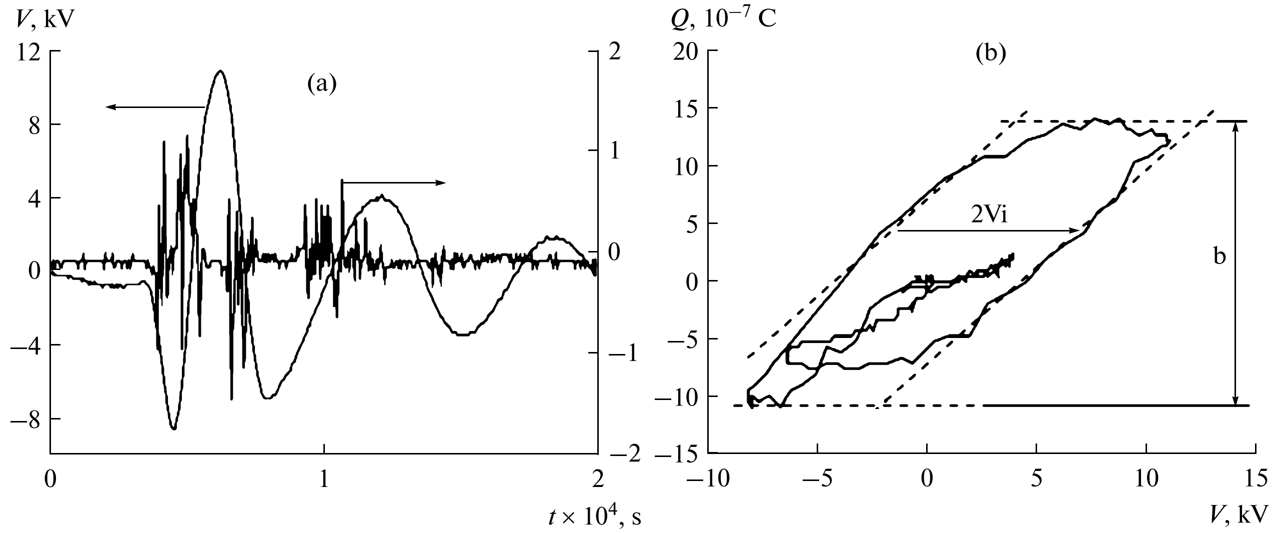

Fig. 2. Characteristics of barrier discharge: (a) high-voltage pulse and discharge current and (b) charge–voltage curve.

hexadiene, ethynylbenzene, and styrene were also detected in small amounts among the products.

At a benzene flow rate of 0.24 cm^3/min, the amount of SPC is 79.7 wt % and that of IPC is 0.9 wt %. The formation of IPC occurs over the entire surface of the electrodes. An increase in benzene flow rate to 0.4 ml/min leads to the disappearance of IPC from the products. The selectivity of formation of SPC is almost independent of the flow rate of benzene, although the conversion decreases from 8.8 to 2.7 wt% with the increasing flow rate.

Table 1. Product composition for transformation of a benzene vapor and argon mixture in the barrier-discharge reactor at different flow rates of benzene

Products	Benzene flow rate, cm^3/min			
	0.24	0.4	0.74	1
	Amount, wt %			
Toluene	0.5	0.8	1.0	0.7
Ethylbenzene	1.3	1.3	1.0	1.1
Cumene	0.2	0.2	0.2	0.2
Propylbenzene	0.3	0.6	0.4	0.4
Cyclohexadienes	1.0	1.7	1.9	1.7
Ethynylbenzene	0.1	0.2	0.1	0.2
Styrene	0.5	0.5	0.5	0.5
Ethylcyclohexadienes	0.5	0.3	0.3	0.3
Phenylcyclohexadienes	6.9	9.0	9.9	8.0
Biphenyl	6.8	7.6	8.4	6.6
SPC	79.7	76.5	75.1	79.4
IPC	0.9	–	–	–
Unidentified*	1.4	1.2	1.1	0.9
Conversion**, wt %	8.8	5.5	3.6	2.7

Notes: * The total amount of unidentified compounds with a low intensity of chromatographic peaks.

** Hereinafter, the values of the conversion per pass of feed mixture through the discharge zone of the reactor and calculated on the basis of the total mass of hydrocarbons passed through the reactor are given.

Ethylene, ethane, and traces of hydrogen were found among the gaseous products. Since the total amount of gaseous products in the gas mixture at the reactor outlet did not exceed 2 vol % in all experiments, we do not present detailed information about them in this paper. An analysis of the IR and NMR spectra of the polymeric products showed that they have a complex crosslinked structure containing fragments of hydrocarbons of various classes. The molecular mass of SPC was found to be ~235 g/mol.

Unfortunately, there is a lack of published experimental data on the mechanism of transformation of hydrocarbons, in particular, benzene directly under the DBD conditions. However, studies devoted to the mechanisms of hydrocarbon transformations in nonequilibrium electric discharges at low pressures have been reported. For example, Slovetskii [8], having surveyed published data and the results of high own research, concluded that at a concentration of vaporized hydrocarbons in mixtures with inert gases above 1 vol %, the main contribution to their decomposition can be due to collisions with electrons that do not lead to ionization. It was shown that benzene primarily generates the phenyl radical under conditions of nonequilibrium electric discharge. Studying the decomposition products of the C_6H_6/Ar mixture in corona discharge (close to DBD in properties) by matrix IR spectroscopy, Bai and Ault [9] also detected the phenyl radical, along with other benzene degradation products. Then, discharge-induced initiation step can be represented by the following simplified set of reactions:

$$C_6H_6 + e \longrightarrow C_6H_5^{\bullet} + H^{\bullet} + e, \tag{1}$$

$$C_6H_6 + e \longrightarrow R^{\bullet} + R'^{\bullet} + e, \tag{2}$$

where e denote discharge electrons and $R^{\bullet}$ and $R'^{\bullet}$ are fragments of the benzene ring.

The radicals generated at the discharge initiation step of the reaction subsequently enter into the combination reaction yielding the products:

$$R^{\bullet} + R'^{\bullet} \longrightarrow R - R'. \tag{3}$$

The repeated exposure of the products to DBD leads to their further transformation into polymer-like compounds.

We assumed that the replacement of argon by hydrogen can reduce the yield of the products of benzene polymerization in DBD because of the occurrence of the competing reaction between atomic hydrogen, formed by the action of DBD on molecular hydrogen,

$$H_2 + e \longrightarrow 2H^{\bullet} + e \tag{4}$$

and the benzene ring fragment:

$$R^{\bullet} + H^{\bullet} \longrightarrow RH. \tag{5}$$

Table 2 shows the results of experiments on the conversion of benzene vapor in the presence of hydrogen.

Indeed, the formation of IPC is not observed during the conversion of benzene in the presence of hydrogen. At as low a benzene flow rate as 0.08 ml/min, the amount of SPC in the reaction products (61.4 wt %) is below that in the case of C_6H_6/Ar mixture at a benzene flow rate of 0.24 cm^3/min (79.7 wt %). The amounts of cyclohexadienes, biphenyl, and alkylbenzenes in the products are 16, 10.2, and 1.5 wt %, respectively. The degree of conversion is 4.5 wt %.

On the basis of reactions (1)–(3), it might be expected that the transformation of the benzene–PBM mixture would lead to the formation of alkylbenzenes, valuable preproducts for organic synthesis:

$$RH + e \longrightarrow R^{\bullet} + H^{\bullet} + e, \tag{6}$$

$$C_6H_5^{\bullet} + R^{\bullet} \longrightarrow C_6H_5 - R, \tag{7}$$

where RH is the alkane molecule.

By analogy with experiments in argon, the experiments in the propane–butane mixture were also conducted at different benzene flow rates. The initial PBM contained 65.4 vol % propane, 19.5 vol % butane, and 7.5 vol % isobutane. The results are presented in Table 3.

It is seen that alkanes (to 20.5 wt%, mainly of isomeric structure) are produced in addition to alkylbenzenes (up to 38.5 wt %). An increase in benzene flow

Table 2. Product composition for transformation of a mixture of benzene vapor and hydrogen in a barrier-discharge reactor (benzene flow rate of 0.08 cm^3/min)

Products	Amount, wt %
Cyclohexadienes	1.5
Toluene	0.7
Ethylbenzene	0.5
Ethynylbenzene	0.3
Styrene	0.4
Cumene	0.2
Ethynylbenzene	0.1
Propylbenzene	0.1
Ethylcyclohexadienes	0.1
Phenylcyclohexadienes	14.3
Biphenyl	10.2
IPC	61.4
SPC	–
Unidentified	10.1
Conversion, wt %	4.5

Table 3. Product composition for the transformation of a benzene vapor–PBM mixture in DBD at different benzene flow rates

Products	Benzene flow rate, cm^3/min		
	0.08	0.24	0.4
	Amount, wt %		
Pentanes	2.1	2.6	8.6
Hexanes	4.4	2.3	6.4
Heptanes	1.1	0.8	5.5
Octanes	0.4	0.4	–
Cyclohexadiene	1.6	2.7	6.3
Toluene	5.1	10.2	17.2
Ethylbenzene	4.6	4.1	5.3
Cumene	6.9	1.3	11.2
Propylbenzene	2.5	0.5	3.8
Isobutylbenzene	1.2	6.6	1.0
Ethynylbenzene	0.7	2.5	0.8
Styrene	0.8	3.3	1.2
Ethylcyclohexadienes	2.4	1.1	5.1
Propylcyclohexadiene	0.6	1.4	1.1
Isobutylcyclohexadiene	0.4	0.1	–
Phenylcyclohexadienes	1.4	7.6	3.2
Diphenyl	2.6	7.9	8.6
SPC	56.7	33.0	9.1
IPC	–	–	–
Unidentified	4.5	11.6	5.6
Conversion, wt %	3.8	3.1	0.6

rate reduces the amount of SPC in the products from 56.7 to 9.1 wt %.

In summary, the example of transformation of the C_6H_6–PBM mixture allowed us to find conditions at which the yield of the traditional polymerization products formed in dielectric-barrier discharge is significantly reduced and to show the feasibility of manufacturing liquid alkylbenzenes and isoalkanes.

REFERENCES

1. O. Godoy-Cabrera, R. Lopez-Callejas, R. Valencia, and S.R. Barocio, Braz. J. Phys. **34**, (4B), 1766 (2004).
2. A. K. Pikaev, High Energy Chem. **34**, 47 (2000).
3. M. W. Ranney and W F. O'Connor, J. Am. Chem. Soc. **80**, 297 (1969).
4. J. K. Stille, R. L. Sung, and K. J. Vander, J. Org. Chem. **30**, 3116 (1965).
5. S. V. Kudryashov, G. S. Shchegoleva, E. E. Sirotkina, and A. Yu. Ryabov, High Energy Chem. **35**, 120 (2001).
6. V. G. Samoilovich, V. I. Gibalov, and K. V. Kozlov, *Physical Chemistry of Barrier Discharge* (Mosk. Gos. Univ., Moscow, 1989) [in Russian].
7. N. N. Abryutina, V. V. Abushaeva, O. A. Aref'ev, et al., *Modern Techniques of Petroleum Research*, Ed. by A. I. Bogomolov, M. B. Temyanko, and L. I. Khotyntseva (Nedra, Leningrad, 1984) [in Russian].
8. D. I. Slovetskii, Khim. Plazmy, issue 8, 189 (1981).
9. H. Bai and B. S. Ault, J. Phys. Chem. **96**, 9169 (1992).