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BRIEF COMMUNICATIONS

## Oxidation of Propylene and Isobutylene in a Reactor with Barrier Discharge

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**Abstract**—The oxidation of propylene and isobutylene in barrier-discharge plasma in the presence of octane was studied. The possible reaction mechanism was considered.

Recently, the interest in organic synthesis in electric discharges has been increasing. However, development of new technologies based on electric discharges is hindered by the lack of a sufficiently large body of data on the mechanisms and kinetics of conversion of organic compounds in plasma, which is, as a rule, caused by the low selectivity of the occurring reactions, tarring, and deep degradation of organic molecules.

We have shown previously that oxidation of hydrocarbons belonging to various classes without formation of tars and products of complete oxidation is possible in a barrier discharge [1]. This is achieved by effective removal of reaction products from the zone of the barrier discharge with a hydrocarbon film formed by condensation of supersaturated vapor of a hydrocarbon on the cooled reactor walls. For example, oxidation of hexane, cyclohexane, and cumene mainly yields hydroxy and carbonyl compounds: alcohols, aldehydes, and ketones with the same number of carbon atoms as that in the starting compound. The product formed in oxidation of cyclohexene is epoxycyclohexane (62 wt %).

It was shown in [2] that the selectivity of cyclohexene oxidation can be, in principle, controlled. The maximum yield of cyclohexene oxide was  $\sim$ 72%. However, products of oxidation of light olefins are of greater importance for petrochemical synthesis.

In this work we studied oxidation of propylene (PR) and isobutylene (IB) in a reactor with a barrier discharge.

## EXPERIMENTAL

PR and IB were oxidized in the presence of octane to create a hydrocarbon film in which reaction prod-

ucts are dissolved and are thereby removed from the zone of the barrier discharge. A flow-through gasdischarge reactor of coaxial design was used. The experimental setup has been described in detail previously [1].

The starting parameters of the process were as follows: flow rate of oxygen, olefin, and octane through the reactor 3.0, 0.6, and  $6 \times 10^{-3}$  l h<sup>-1</sup>, respectively; temperature of the reactor walls 10°C; atmospheric pressure; amplitude of voltage pulses 12 kV; pulse repetition frequency 500 Hz; specific energy of the discharge 1.3 Wh l<sup>-1</sup>.

The liquid reaction products were analyzed by gas chromatography: heat-conductivity detector in the isothermal mode at 120°C; 1.2-m-long packed column with an inner diameter of 3 mm; sorbent Porapak-Q; carrier gas helium.

The conversions and the composition of products formed in oxidation of PR and IB are listed in the table. It can be seen that the main reaction products are the corresponding epoxides. In contrast to the oxidation of cyclohexene, the oxidation of PR and IB is accompanied by degradation of the olefin molecule to give methanol and formaldehyde. At the same time, no CO, CO<sub>2</sub>, acids, or tarring products were found in the reaction products, which constitutes a fundamental difference between the results of this study and those of previous studies of oxidation of light olefins in electric discharges [3–5].

It should be noted that octane is oxidized simultaneously with the olefins. The conversion of octane is  $\sim 0.5$  wt % in both cases. As a result, hydroxy and carbonyl compounds characteristic of octane oxidation products are formed [6].

A possible mechanism of cyclohexene oxidation

was suggested in [2]. In this mechanism, the reaction products are formed by two pathways. The first of them yields cyclohexene oxide, cyclohexanone, and cyclopentylmethanal, and the second, cyclohexenone, cyclohexenol, and bicyclohexenyl.

No unsaturated oxygen-containing compounds were found in oxidation products of PR and IB, which suggests that the reaction predominantly goes by the first pathway involving activation of oxygen molecules by electron impact. This can be attributed to the higher dissociation energies of PR and IB molecules, compared with those of cyclohexene and oxygen molecules [7].

By analogy with the previously suggested mechanism of cyclohexene oxidation, the possible mechanism of PR oxidation can be represented as

$$H_{2}C=CHCH_{3} + O(^{3}P) \xrightarrow{k_{1}} H_{2}C \xrightarrow{O} CHCH_{3}^{*},$$

$$H_{2}C \xrightarrow{O} CHCH_{3}^{*} \xrightarrow{k_{2}} H_{3}C \xrightarrow{O} CHCH_{3}^{*},$$

$$H_{2}C \xrightarrow{O} CHCH_{3}^{*} \xrightarrow{k_{2}} H_{3}C \xrightarrow{O} CHCH_{3}^{*},$$

$$H_{2}C \xrightarrow{O} CHCH_{3}^{*} \xrightarrow{K_{1}} H_{3}C \xrightarrow{O} CHCH_{3}^{*} \xrightarrow{K_{1}} H_{3}^{*} \xrightarrow{K_{1}} H_{3}^{*}$$

Acetaldehyde, formaldehyde, methanol, and water are formed by decomposition of a "hot" molecule of propylene oxide, with the resulting fragments subsequently involved in radical reactions. In the case of cyclohexene oxidation, the hot molecule of olefin oxide does not decompose [1, 2].

The validity of the suggested mechanism of PR and IB oxidation can be verified by simple calculations. For the oxidation of olefins, which occurs in a reactor with a steady flow mode, the following expression is valid:

$$w_1/w_2 = X_1/X_2, (1)$$

where  $w_1$ ,  $w_2$ ,  $X_1$ , and  $X_2$  are the oxidation rates and conversions of PR and IB, respectively.

In terms of the oxidation mechanism suggested, the following expression can be written for the oxidation rate of PR:

$$w_1 = d[C_3H_5]/d\tau = k_1[O(^3P)][C_3H_6].$$
 (2)

A similar expression can be written for  $w_2$ .

At a constant discharge power and all other experimental conditions being the same, the rates of

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Conversions X and composition of products formed in oxidation of PR and IB\*

| Olefin           | X, wt % | Oxidation products   | Selectiv-<br>ity, wt %              |
|------------------|---------|--|-------------------------------------|
| Propylene        | 1.56    | Propylene oxide<br>Acetone<br>Acetaldehyde<br>Methanol<br>Water + formaldehyde       | 43.3<br>30.9<br>10.2<br>3.4<br>12.2 |
| Isobutyl-<br>ene | 6.74    | Isobutylene oxide<br>2-Methylpropanal<br>Acetone<br>Methanol<br>Water + formaldehyde | 43.8<br>23.9<br>19.2<br>4.6<br>8.5  |

\* Conversion obtained in a single pass of the starting mixture through the reactor at a time of contact with the discharge zone equal to  $\sim 10.5$  s.

generation of atomic oxygen in mixtures of oxygen with PR and IB will be the same, because their molecules have close cross sections of electron energy scattering. Therefore, the composition of the gas mixtures has no effect on the average electron energies. Hence, expression (1) can be written as

$$k_1'/k_1'' = X_1/X_2, (3)$$

where  $k_1$  and  $k_1^{"}$  are the rate constants of interaction of atomic oxygen with PR and IB, respectively. The results of calculation by expression (3) are given below:

$$\frac{k'_1}{k''_1} = \frac{2.2 \times 10^{12} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}}{2.2 \times 10^{13} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}} = 0.183 \ [8],$$
$$X_1/X_2 = 1.56/6.74 = 0.231.$$

It can be seen that the calculation results reasonably agree with the experiment. The calculation error is 20.9%.

## CONCLUSION

Oxidation of propylene and isobutylene by oxygen in the plasma of a barrier discharge allows synthesis of oxides of light olefins without formation of tars or complete oxidation.

## REFERENCES

 Kudryashov, S.V., Shchegoleva, G.S., Sirotkina, E.E., and Ryabov, A.Yu., *Khim. Vys. Energ.*, 2000, vol. 34, no. 2, pp. 145–148.

- Kudryashov, S.V., Ryabov, A.Yu., Shchegoleva, G.S., and Sirotkina, E.E., in *Materialy V mezhdunarodnoi* konferentsii "Khimiya nefti i gaza" (Proc. V Int. Conf. "Chemistry of Oil and Natural Gas"), Tomsk, September 22–26, 2003, p. 485.
- Weisbeck, V.R., Chem. Ber., 1972, vol. 76, no. 11, pp. 1147–1155.
- Junichi, I., Kazuto, T., and Satoru, T., Bull. Chem. Soc. Jpn., 1977, vol. 50, no. 8, pp. 2183–2184.
- 5. Lyaskin, Yu.G., Mazanko, A.F., and Reznichenko, N.I.,

Khim. Vys. Energ., 1983, vol. 17, no. 4, pp. 352-357.

- Kudrjashov, S.V., Loos, D.A., and Sirotkina, E.E., *Contributed Papers, Int. Symp. on High Pressure Low Temperature Plasma Chemistry HAKONE VII*, Griefswald (Germany), September 10–13, 2000, vol. 2, p. 257.
- *Khimiya plazmy* (Chemistry of Plasma), Smirnov, B.M., Ed., Moscow: Energoizdat, 1981, issue 8.
- 8. Herron, J.T. and Huie, R.E., J. Phys. Chem. Ref. Data, 1973, vol. 2, no. 3, pp. 465–514.