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A. P. RUDENKO, D. E. BODRINA, Academician A. A. BALANDIN,
M. F. RODICHEVA

ALKYLATION OF BENZENE BY A CARBONACEOUS SUBSTANCE OBTAINED FROM PROPYLENE ON SILICA GEL

It was shown earlier that in the process of polycondensation of propylene with the formation of a carbonaceous and resinous substance on silica gel, along with other reactions, an elementary stage of demethanation takes place ([1]); moreover, under the conditions of dehydration of isopropyl alcohol in the temperature range 700–775°, propylene polycondenses with the formation of carbides corresponding to the empirical formula $(C_1H_{1.5})x$, which, upon prolonged heating at the same temperatures, are converted into substances poorer in hydrogen, $(C_1H_{0.4})x$. Assuming one and the same mechanism of carbide formation in both cases, the differences in their composition can be explained by the fact that the carbide $(C_1H_{1.5})x$ is an exhaustively methylated hydroaromatic form with the same complex polycyclic carbon skeleton as the carbide $(C_1H_{0.4})x$, which represents an aromatic form. The transition from the first form to the second is possible as a result of demethanation and dehydrogenation.

Since, in the process of demethanation of carbides, their increased reactivity toward methylation of aromatic hydrocarbons could be expected, we carried out the corresponding experiments.

By the procedure described earlier ([2–5]), 1-hour experiments were conducted in a flow system on KSM silica gel at temperatures of 500–900° with pure propylene obtained by dehydration of isopropyl alcohol; with pure benzene; with an equimolar mixture of propylene and benzene vapors; in addition, experiments were carried out with benzene on silica gel preliminarily carbonized with an equimolar amount of propylene. The initial reactants were chromatographically pure. For each experiment, 5 ml of fresh silica gel was taken; the feed rate was 0.08 mol/hr for propylene and 0.13 mol/hr for benzene. The yields of carbonaceous substance were determined by weighing the reactor. The gaseous and liquid catalyzates were analyzed on gas-adsorption and gas-liquid chromatographs. For gas analysis, columns with 5A zeolite and alumina were used; the mobile phase was helium and nitrogen. For analysis of liquid catalyzates, a column with dinonyl phthalate on diatomite (15%) was used; the mobile phase was helium. Elemental analysis of the carbonaceous substance on the catalyst was carried

Figure 1

Figure 1: Figure 1

out with the aid of a chromatographic apparatus that made it possible to determine C and H from CO_2 and H_2, with an accuracy for hydrogen of $\pm$0.01%. In the text, the results of such analyses are given as atomic ratios H/C.

The data obtained on the course of the processes of carbon and resin formation (Fig. 1) correspond to analogous data under the conditions of dehydration of isopropyl alcohol ([1]), and under the conditions of benzene decomposition ([2-4]). In the decomposition of propylene, formation of liquid catalyzate was not observed. In the catalyzate from experiments with pure benzene, no toluene was detected over the entire temperature range investigated. In experiments with a mixture of benzene vapors and propylene, toluene is formed with a maximum yield at 750° (Fig. 2), as well as a certain amount of higher alkylation products, appearing on the chromatograms after cumene, up to cymene.

It may be assumed that the alkylation of benzene proceeds not by carboids formed from propylene, but by some other mechanism, for example, according to (6), through reaction with methylene radicals in the vapor phase. To test this, a series of experiments was carried out with separate passage of propylene and benzene. In these experiments, the silica gel was first carbonized with propylene; then the apparatus and the carbonized catalyst were flushed at the experimental temperature with pure nitrogen until the traces of propylene had completely disappeared

Fig. 1. Course of carbon formation (a) and resin formation (b) as a function of temperature in experiments with propylene (1), benzene (2), a mixture of 0.08 mole of propylene and 0.13 mole of benzene (3) on silica gel, and with benzene (4) on silica gel previously carbonized with propylene (yields are given in grams, calculated per 0.1 mole of the initial hydrocarbon)

(as monitored chromatographically); after flushing, an experiment with benzene was carried out at the same temperature. During the experiment, samples of the liquid catalyst were taken and analyzed after 3-5, 10, 20, and 60 min. Toluene, *p*-xylene, and cumene were found in the catalyst (Fig. 2a).

The alkylation of benzene by carboids in this case is also confirmed by the sharp decrease in the average content of toluene, xylene, and cumene in the catalyst as a function of time from the start of benzene passage; this is due to the fact that all the toluene and other alkylation products are formed during the first 20-30 min of the experiment, while subsequently only dilution of the catalyst by unreacted benzene occurs (Fig. 2b). The decrease in the yields of alkylation products evidently occurs in accordance with the decrease in the number of methyl and propyl groups present on the carbonized catalyst and consumed in alkylation.

From the yields of alkylation products (Fig. 2a) and the data on the amount of carbonaceous material deposited on silica gel in experiments with pure propylene (Fig. 1), it is possible to calculate the content of alkylating methyl and propyl groups in the carbonaceous material at different temperatures. At temperatures below 600°, the content of methyl groups in the carbonaceous material on the catalyst (Fig. 2a) is highest; at higher temperatures their relative content decreases, down to fractions of a percent at 800°, and simultaneously the hydrogen content also decreases. Thus, if at temperatures below 600° the ratio of the number of hydrogen atoms to carbon atoms in the carbonized catalyst is ~2, then at 625° it is already 1.03, at 675° it is 0.78, and at 775° it is 0.74.

Comparing the data of Fig. 2 for experiments with benzene on carbonized silica gel and the yields of carbonaceous material in experiments with propylene (Fig. 1), it may be concluded that 600° is the upper temperature

limit of stability of polypropylenes $(C_1H_2)_x$ and methylated hydroaromatic carbides that are part of the carbonaceous deposits. This is confirmed by data on the sharp increase in the content of hydrogen and methane in the contact gases in experiments with propylene above 600° (see Table 1) and by elemental analyses of the carbonaceous substances. In this connection, the increase in the yields of toluene as the temperature rises to 600° is evidently associated with an increase in the yields of the carbonaceous substance, while the fall in the yields of toluene above 600° is associated with a sharp decrease in the content of methyl groups in the carbonaceous substance, not compensated by the increase in the yields of the carbonaceous substance.

Fig. 2. Alkylation of benzene by the carbonaceous substance obtained from propylene on silica gel. **a**—Temperature dependence of the yields of alkylation products in grams per 0.1 mole of initial propylene: 1—toluene in experiments with a mixture of propylene and benzene on silica gel; 2—toluene, 3—cumene, 4—*p*-xylene in experiments with benzene on silica gel preliminarily carbonized with propylene. Temperature dependence of the content of methyl (5) and propyl (6) groups in the carbonized propylene catalyst, in percent by weight of the carbonaceous substance. **b**—Change in the content of alkylation products in the catalyst as a function of time in an experiment with benzene on preliminarily carbonized silica gel at 625° (curves for other temperatures have a similar character). Average content of toluene (1), cumene (2), and *p*-xylene (3). Change in the content of toluene in separately collected samples during the course of the experiments (4).

The existence of a maximum in toluene formation when the reactants are passed jointly at 750° can be explained by the reduced stability of the methyl groups in toluene and by their hydrogenolysis at higher temperatures, which agrees with previously obtained data on the processes of dehydrocondensation of benzene homologues on silica gel at high temperatures (3). The formation of other alkylation products (xylenes, higher alkylbenzenes, and cumene) along with toluene may be associated with successive methylation of benzene and with the use, as alkylating groups, of larger fragments of the carbonaceous substance.

The mechanism of alkylation of benzene by methylated hydroaromatic carbides bound to the surface of silica gel may be represented by the scheme

$$\text{carbide–CH}_3 + \text{C}_6\text{H}_6 \longrightarrow \text{carbide–CH}_2\text{–C}_6\text{H}_5 \longrightarrow \text{carbide–H}_2 + \text{H}_3\text{C–C}_6\text{H}_5$$

$$\text{carbide} + \text{H}_3\text{C–C}_6\text{H}_5 \longleftarrow \text{carbide–CH}_2\text{–C}_6\text{H}_5 + \text{H}_2 \downarrow$$

$$[\text{carbide} + \text{H}_3\text{C–C}_6\text{H}_5]$$

All the results obtained prove the existence of alkylating properties in the carbonaceous substance formed during the polycondensation of propylene on silica gel below 800°; on the other hand, they also confirm the correctness of the mechanism of resin and carbon formation proposed in (1), which admits the existence of demethanation as an elementary stage in the polycondensation of propylene.

Table 1

Composition of gas from catalysis in experiments with propylene on silica gel (series I), with a mixture of propylene and benzene vapors on silica gel (series III), and with benzene on silica gel previously carbonized with propylene (series IV)

Series of experiments	Temperature, °C	H_2	CH_4	C_2H_3	C_2H_4	C_3H_6
I	525	2.9	5.5	Traces	6.4	85.0
I	570	5.4	6.6	2.1	11.7	74.0
I	625	18.0	35.8	2.2	16.0	34.2
I	650	16.3	48.6	3.9	19.3	11.3
I	675	16.2	54.0	4.2	21.0	5.2
I	700	28.4	51.4	2.5	14.5	3.1
I	775	44.4	48.2	1.4	4.1	0
I	840	51.4	45.0	0	2.8	0
III	507	0	0.9	0	1.2	97.0
III	600	0	5.0	0	1.2	93.0
III	668	17.0	37.0	2.2	22.4	18.3
III	850	92.6	7.2	0	0	0
IV	507	82	0	0	0	18.0
IV	600	90.4	2.0	0	4.0	3.6
IV	668	76.0	22.8	0	Traces	Traces
IV	800	96.2	3.6	0	0	0

An analogous effect of alkylation of benzene by carbonaceous substance apparently occurs in the cracking of cumene, as indicated by data on the presence of

toluene and xylenes in the cracking products (3). The reactions of coupled alkylation of aromatic hydrocarbons on aluminosilicates in dealkylation processes can probably be explained by the same effect of alkylation by carbonaceous substance (7, 8). Alkylating properties may also be expected in carbonaceous substances obtained during the polycondensation of ethylene and acetylene, in the course of whose formation an elementary demethanation stage has also been noted (9), and in certain other cases. Alkylation of aromatic hydrocarbons may serve as a convenient method for detecting methyl and other groups in alkylating carbides and for establishing their composition and structure.

The existence of alkylating properties in certain types of carbonaceous substance deposited on catalysts in organic reactions compels a critical attitude toward the existing concepts of the mechanism of catalytic cracking and hydrogen redistribution and toward explanations of individual facts. In particular, the fact that toluene, *p*-xylene, and other alkylation products are formed during the dehydrogenation of cyclohexane on metallic catalysts—explained, as is known (6), by reactions involving free methylene radicals—may, in the light of the present work, receive another explanation, through the alkylating properties of carbides formed on the catalyst surface. Therefore analogous facts can no longer be regarded as unambiguous evidence in favor of the existence and active role of free methylene radicals in chemical processes, and will require further investigation by other methods.

Moscow State University
named after M. V. Lomonosov

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REFERENCES

1. A. A. Balandin, A. P. Rudenko, G. Stegner, DAN, **129**, 565 (1959).
2. A. P. Rudenko, *Vestn. Moskovsk. univ., ser. khim.*, No. 5, 69 (1960).
3. A. P. Rudenko, A. A. Balandin, I. I. Gradchenko, *Izv. AN SSSR, OKhN*, 1960, 605.
4. A. P. Rudenko, A. A. Balandin, G. Yu. Chev, *Izv. AN SSSR, OKhN*, 1961, 164.
5. A. P. Rudenko, in: *Kataliz v Vysshei shkole*, Part II, Moscow, 1962, p. 72.
6. N. D. Zelinskii, N. I. Shuikin, DAN, **3**, 255 (1934).
7. A. V. Topchiev, G. M. Mamedaliev et al., DAN, **112**, 1071 (1957).

8. G. M. Mamedaliev, Yu. G. Mamedaliev, A. V. Topchiev, *Izv. AN SSSR, OKhN*, 1958, 91.

9. A. P. Rudenko, A. A. Balandin, M. M. Zabolotnaya, *Kinetika i kataliz*, **2**, 440 (1961).

Note: Figure translations are in progress. See original paper for figures.