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# ALKYLATION OF TOLUENE WITH PROPYLENE OVER THE ELECTRON DONOR-ACCEPTOR COMPLEXES OF AROMATIC HYDROCARBONS WITH SODIUM

Susumu TSUCHIYA, Yoshiaki SAITO, Tsugio MURAKAMI,
Hideaki IWATA, and Tsutomu ANNAKA
Department of Industrial Chemistry, Faculty of Engineering,
Yamaguchi University, Tokiwadai, Ube, Yamaguchi 755

The alkylation of toluene with propylene takes place over the electron donor-acceptor complexes of anthracene, chrysene, benzoquinone, and p-chloranil with sodium, and two types of the alkylation, the side-chain- and the nuclear-alkylation, have been suggested by the reaction products, butylbenzenes and cymenes.

Heterogeneous catalysis by electron donor-acceptor (EDA) complexes has extensively been investigated since Kondow et al.1) found that the hydrogen-deuterium equilibration reaction was catalyzed by a tetracyanopyrene-cesium complex. The types of reactions so far investigated, however, are limited to the hydrogen-deuterium exchange and equilibration, to the hydrogenation and to the double bond shift reaction.2) In the present work, the alkylation of toluene with propylene over the EDA complexes of various aromatic hydrocarbons with sodium has been investigated in order to extend the catalytic application of EDA complexes.

A usual flow type system with a by-pass at atmospheric pressure was employed to follow the reaction, where helium was used as a diluent agent. The EDA complexes, the catalysts, similarly prepared beforehand in a vacuum system to that described previously,3) were brought to be fixed in the system. The helium stream with toluene and propylene was initially passed through the by-pass way, and then introduced into the reactor by changing the flow to start the reaction. The amounts of toluene and propylene, simultaneously admitted into the helium stream, were occasionally measured before the reactor. After stopping the feed of reactants, helium stream was still passed over the catalyst for a while. Accordingly, the unreacted toluene, the reaction products, and perhaps the species weakly adsorbed on the catalyst, could be condensed by a dry ice trap after the reactor. They were analyzed by gas chromatography, the analytical conditions of which are similar to that described by Yashima et al.4)

The reaction of toluene with propylene did not take place over either of the components of the EDA complexes of anthracene, chrysene, p-chloranil, and benzoquinone with sodium up to 150°C, but proceeded over the EDA complexes even at 25°C. Over benzoquinone-sodium complex, however, the reaction could not be measured above 90°C, because the complex was easily decomposed at higher temperature. Table 1 shows typical results for the reaction of toluene with propylene over the EDA complexes. The ratios, (helium)/(toluene + propylene), propylene/toluene, and (weight of catalyst)/(feed rate of toluene + propylene + helium), the parameter of contact time, were 30 (mole/mole), 20 (mole/mole), and 5 (g/mole·hr$^{-1}$), respectively. No other gaseous hydrocarbon than propylene could be detected in the helium stream after the dry ice trap.

Table 1. Reaction of toluene with propylene over various EDA complexes

| Acceptor of EDA complexes | anthracene | | chrysene | | p-chloranil | | benzoquinone |
|---|---|---|---|---|---|---|---|
| Reaction temperature °C | 100 | 95 | 110 | 90 | 100 | 25 | 25 |
| Composition of aromatic compounds % | | | | | | | |
| toluene unreacted | 36 | 40 | 44 | 67 | 84 | 96 | 97 |
| benzene and xylenes | 13 | 10 | 0 | 0 | 8 | 3 | 2 |
| cymenes | 0 | 0 | 56 | 33 | 3 | 1 | 1 |
| butylbenzenes | 51 | 50 | 0 | 0 | 2 | 0 | 0 |
| others | 0 | 0 | 0 | 0 | 3 | 0 | 0 |

The reaction products distribution suggests that anthracene- and chrysene-sodium complexes are much more active and selective catalysts for the alkylation of toluene with propylene than p-chloranil- and benzoquinone-sodium complexes. Benzene and xylenes probably are formed by the disproportionation of toluene, while butylbenzenes and cymenes are formed by the side-chain-alkylation and by the nuclear-alkylation of toluene with propylene, respectively. The reaction products thus depend upon the acceptor of the EDA complexes.

The butylbenzenes given by the anthracene-sodium complex were only tert- and sec-butylbenzene, and the ratio, tert/sec was about 4. The results seemingly do not agree with the classical work by Pines et al.[5] that isobutylbenzene was formed by the alkylation of toluene with propylene in the presence of sodium and anthracene. In their experiments, anthracene-sodium complex of catalytic activity might be formed in the reaction system, but the reaction was carried out in an autoclave under such severe conditions as 297°C and 90 atm. Our results obtained by the experiments under mild conditions, accordingly, could be approved, considering the different experimental conditions.

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