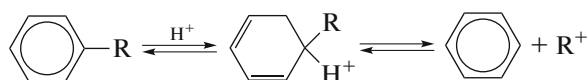


Table 1. Relative rates of hydrodealkylation [6–8]

| Compound | Catalytic process | | | | Thermal process | | |
|----------------------------------------|-------------------|-----|-----|-----|-----------------|-----|-----|
| | | | | | | | |
| Toluene | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 |
| <i>m</i> -Xylene | 2.6 | – | 1.2 | 2.3 | – | 3.5 | 1.5 |
| <i>p</i> -Xylene | 2.4 | – | 2.1 | – | 1.5 | 2.9 | – |
| <i>o</i> -Xylene | 4.6 | – | 3.5 | – | 2.5 | 6.4 | 0.8 |
| Mixture of C ₈ hydrocarbons | – | 2.7 | – | – | – | – | – |
| 1,3,5-Trimethylbenzene | – | – | 1.9 | 4.2 | – | – | 3.4 |
| 1,2,4-Trimethylbenzene | – | – | 2.9 | – | – | – | – |
| 1,2,3-Trimethylbenzene | – | – | 5.4 | – | – | – | – |
| Mixture of C ₉ hydrocarbons | – | 4.4 | – | – | – | – | – |

tion of a σ complex, which is then transformed as follows in benzene



With increase in the number of carbon atoms and the branching of the alkyl radicals, the alkyl carbonic ion formed becomes more stable, and hence the dealylation rate should increase.

In fact, the relative dealylation rate does increase with increase in the number of substituents and the number of carbon atoms in the substituents (Table 1), as established in numerous kinetic studies of the hydrodealkylation of monocyclic aromatic hydrocarbons [6–8].

In our view, the reactivity of individual methylbenzenes is primarily determined by their structure and the electron-density distribution in the ring.

In xylenes, superposition of the conjugation of two methyl substituents is accompanied by increase in the

electron density at carbon atoms in the *o* and *n* positions of the ring. That facilitates the formation of an intermediate carbon complex with catalytic properties. As a result, the demethylation is greatest when using *o*-xylene and least when using *n*-xylene.

The influence of induction and conjugation on the rate constants of hydration was established for various organic compounds in [8]. In the case of trimethylbenzenes, as a result of conjugation of the methyl substituents with the aromatic ring, the electron density of 1,3,5-trimethylbenzene is shifted to the 2,4,5 position. That explains why it has the greatest relative rate of hydration among the trimethylbenzenes and the lowest rate of demethylation. The following explanation was offered for the maximum rate of demethylation of 1,2,3-trimethylbenzene and the ease of splitting of the methyl substituent from position 2 in [8]: the shift in the electron density due to induction is equal to the shift in the electron density due to conjugation.

In the thermal process, other behavior associated with the specific mechanism is observed, but it falls outside the scope of the present study.

In the present work, we focus on the action of water vapor (steam) in the high-temperature hydrogenation of a preliminarily purified mixture of raw coke-plant benzene and the naphthalene fraction (boiling at 180–230°C) of semicoking tar from Shubarkol coal.

In the experiments, we use a 3 : 1 (by mass) mixture of raw coke-plant benzene and the naphthalene fraction ($t_{bo} = 180\text{--}230^\circ\text{C}$) from AO Sary Arka Spetskoks (Karaganda, Kazakhstan). Tables 2 and 3 present the characteristics of the naphthalene fraction and raw benzene, respectively.

A high-pressure flow-through laboratory hydrogenation system (reactor volume 0.25 dm³) is employed, with a built-in mixing unit (Fig. 1). The reagent mixture, with added ground catalyst, is placed in the reactor, after preliminary flushing with argon at an initial pressure of 4 MPa. The reactor is heated and, at 150°C, the mixing unit is turned on. The temperature is measured by a thermocouple and maintained automatically to within $\pm 2^\circ\text{C}$. The group hydrocarbon

Table 2. Composition of naphthalene fractions with $t_{bo} = 180\text{--}230^\circ\text{C}$ (wt %)

| Characteristic | Value |
|---------------------------------------------------|--------|
| Density ρ_4^{20} | 0.9358 |
| Iodine number, g J ₂ /100 g of product | 13.4 |
| Sulfur content | 0.32 |
| Monocyclic aromatic hydrocarbons | 31.3 |
| including ethylbenzene | 0.7 |
| Tetralin | 0.6 |
| Methyletalin | 0.5 |
| Naphthalene | 41.5 |
| 2-Methylnaphthalene | 12.4 |
| 1-Methylnaphthalene | 9.2 |
| Benzothiophene | 3.7 |
| Diphenyl | 0.8 |