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Abstract

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COMPARATIVE STUDY OF THE KINETICS OF THE TRANSFORMATIONS OF BENZENE AND ITS HOMOLOGS C_7–C_8 UNDER THE ACTION OF STEAM ON A NICKEL-CHROMIUM CATALYST

In previous papers by two of the authors of the present communication, the dealkylation of benzene homologs ([1,2]), phenol ([3,4]), pyridine ([5]), and thiophene ([6]) under the action of steam on nickel catalysts was studied. Certain conditions were investigated for the selective course of these reactions ([7,8]), which for monodealkylation can be represented by the general equation:

$$RC_nH_{2n+1} + nH_2O \longrightarrow nCO + 3nH_2 + RH, \quad (1)$$

where R = C_6H_5-, *o*-, *p*-, *m*-$CH_3C_6H_4-$, *o*-, *p*-, *m*-HOC_6H_4-, 2-, 3-, 4-C_4H_4N-, etc. Carbon monoxide is apparently (Table 1) the primary product, and in its subsequent reaction with water CO_2 is formed. Similar reactions in the series of benzene homologs of composition C_7—C_9 were also studied in detail in works ([9–13]).

In addition to reaction (1), in parallel ([9–13]) or consecutively ([2]) (depending on the conditions), a reaction of complete cleavage also occurs; for example, for toluene according to the equation

$$C_7H_8 + 7H_2O \longrightarrow 7CO + 11H_2. \quad (2)$$

The comparative study we have carried out of the rates of these reactions under identical conditions on an industrial Ni—Cr_2O_3 catalyst (~ 50% Ni) makes it possible to trace the influence of the structure of the starting substances on the extent of their participation in reactions (1) and (2).

1) The rates of cleavage at one C_{ar}—C_{al} bond under the action of steam (i.e., the rates of monodemethylation) for the hydrocarbons studied and for *m*-cresol in the interval 350–400° form the series: ethylbenzene > *p*-xylene > *m*-xylene > toluene > *o*-xylene, which is analogous to the series derived in work ([3]) only for a temperature of 375° (Fig. 1a). The order of change

in activity does not coincide with the order of change in the equilibrium constants of the corresponding reactions:

Equilibrium constants of reaction (1)	Toluene	Ethylbenzene	Propylbenzene	*o*-Xylene	*m*-Xylene	*p*-Xylene
K_p^{623}	$1.95 \cdot 10^{-1}$	0.71	1.2	2.04	0.89	2.24
K_p^{673}	1.32	20.36	14.6	12.9	5.9	13.3

i.e., the observed activity of hydrocarbons in reaction (1) is determined by kinetic factors. The cleavage of the second methyl group for *m*- and *p*-xylenes is a consecutive reaction. In *o*-xylene, mono- and bis-demethylation are parallel reactions. The ratio of the rates of the parallel reactions of cleavage at the C_{ar}—C_{al} and C_{al}—C_{al} bonds in ethylbenzene, equal on average to 7, is most likely connected

Table 1

Dependence of CO : CO_2 on the feed rate of the starting substances

Temp., °C	Feed rate of starting substances, g-mol $\cdot 10^3$	Substance	CO/CO_2
399	0.88	*o*-Xylene	0.11
399	1.17	*o*-Xylene	0.21
399	1.70	*o*-Xylene	0.30
378	0.85	*p*-Xylene	0.12
378	1.15	*p*-Xylene	0.18
378	1.66	*p*-Xylene	0.25
376	0.86	Ethylbenzene	0.49
376	1.15	Ethylbenzene	0.50
376	1.69	Ethylbenzene	0.79

Table 2

Kinetic constants of the reactions of cleavage of aromatic compounds under the action of steam on Ni–Cr_2O_3

Substance	Reaction	Activation energy, kcal/mol	lg k_0
Benzene	Complete cleavage	17	1.54
Toluene	Demethylation	27	4.98
Toluene	Complete cleavage	32	4.94
Ethylbenzene	Cleavage Cal–Cal	57	14.66
Ethylbenzene	Cleavage Car–Cal	40	9.74
p-Xylene	Monodemethylation	27	4.18
p-Xylene	Bisdemethylation	24	3.34
p-Xylene	Monodemethylation	17	1.68
m-Xylene	Monodemethylation	11	−0.308
m-Cresol	Demethylation	27	3.94

with energy factors—with the ratio of the energies of the bonds arising between the reacting atoms and the catalyst surface.

2) The arrangement of various hydrocarbons, and also of *m*-cresol taken for comparison, in a series according to the rate of cleavage of the nucleus —benzene > *o*-xylene, ethylbenzene, toluene > *p*-xylene, *m*-xylene—may be regarded as a consequence of the influence mainly of steric factors. The position in this series depends on the degree of substitution in the nucleus, i.e., on the relative probability of more or less close contact with the surface.

Multiplet theory uses concepts of the microroughness of catalyst surfaces, assuming that index groups are located on surface projections, next to which there are depressions where non-index substituents can fit ([14]). For unsubstituted benzene the probability of a flat placement on the surface is greatest; for mono- and dimethylbenzenes, correspondingly, it is smaller. The flat arrangement of the benzene nucleus for sextet reactions (and it is precisely by this mechanism that complete cleavage of the nucleus should proceed) was postulated by multiplet theory and subsequently proven (see, for example, ([15])); the flat arrangement of aromatic hydrocarbons during the formation of π-complexes with the surface

Fig. 1. *a*—dependence of the depth of conversion of aromatic hydrocarbons on temperature in the monodealkylation reaction; *b*—the same for the complete-cleavage reaction. 1—benzene, 2—ethylbenzene, 3—*p*-xylene, 4—*m*-xylene, 5—toluene, 6—*o*-xylene, 7—*m*-cresol. m_1—formation of toluene, m_2—formation of benzene.

metals is accepted in works devoted to the development of these ideas (for example, ([16])). *o*-Xylene, in terms of activity in the reaction of complete cleavage, falls into the group of monosubstituted hydrocarbons. This feature may be connected with a certain compactness in the arrangement of the methyl groups in *o*-xylene (bringing the shape of the *o*-xylene molecule closer to that of a monosubstituted molecule), and possibly also with their interaction, the consequence of which is nonplanarity and the associated distortion of the molecule

Fig. 2

Figure 1: Fig. 2

Fig. 3

Figure 2: Fig. 3

and increase in its internal energy.

Fig. 2. Dependence of the ratio CO to CO_2 in the reaction products (1) on temperature.
1 —*m*-cresol, 2 —ethylbenzene, 3 —*p*-xylene, 4 —*m*-xylene, 5 —*o*-xylene, 6 —toluene, 7 —benzene

3) An interesting characteristic of the aromatic compounds studied is their influence on the magnitude of the ratio of CO and CO_2 formed in the reaction with steam (Fig. 2). The degree of this influence depends on the degree of substitution, the length of the side chain, and the presence of hydroxyl in the molecule.

Since the formation of CO_2 is a consecutive reaction (see Table 1), the ratio CO/CO_2 characterizes the relative inhibition of this reaction by the starting substance. Such inhibition cannot be a consequence only of geometrical factors (change in surface coverage with change in molecular size), but is apparently due to the interaction of the molecules with the surface. Ethylbenzene and *m*-cresol are especially strongly chemisorbed by the nickel surface, which may be connected with the presence in one of these molecules of hydroxyl, and in the other of a considerably weakened C_{al}—C_{al} bond, whose dissociation energy is only 63±1.5 kcal/mol ([17]). Since the greatest depth of the most intense reaction —monodemethylation—does not exceed 12%, and the independence of the rate of conversion from contact time indicates an overall zero order of the reaction, we considered it possible to take as the reaction-rate constant the amount of substance converted per unit time ([18]). For conversions of ethylbenzene, the activation energies were calculated from four points in the interval 359-371°, since with further increase in temperature a transition of the reaction into the diffusion region is observed. The high value of the activation energy of dealkylation of ethylbenzene (Table 2) may be connected with the same reason that determines the strong inhibition of conversion of CO into CO_2. The high activity of the C–C bond in the β-position to the benzene ring and of the α-carbon atom are factors determining the statistically average level of the energies of active surface sites for ethylbenzene reactions, which may be lower than

Fig. 3. Logarithmic relationship between the Arrhenius constant for dealkylation reactions of aromatic compounds.
1 —ethylbenzene, cleavage of C_{al}—C_{al}, 2 —ethylbenzene, cleavage of C_{ar}—C_{al}, 3 —toluene; 4 —*o*-xylene, monodemethylation; 5 —*m*-xylene, demethylation; 6 —*o*-xylene, bisdemethylation; 7 —*p*-xylene, monodemethylation; 8 —*m*-xylene,

monodemethylation

for the other hydrocarbons studied. A higher conversion rate is observed at a higher value of the activation energy.

Despite the considerable and, at first glance, irregular fluctuations in the values of the activation energies and the corresponding reaction rates, all the data presented are encompassed by the compensation law (Fig. 3); moreover, this dependence is best obeyed for the cleavage of the C_{ar}—C_{al} bonds in ethylbenzene, toluene, and the para- and meta-xylenes. Deviations are observed for *o*-xylene, the β-C–C bond in ethylbenzene, and the C_{ar}—C_{al} bond in *m*-cresol.

Experimental Part

The kinetics of the reactions described was studied in a semiautomatic flow-type catalytic apparatus using microquantities of the starting substances (1-2 ml) and catalyst (1 ml). In all experiments an industrial nickel–chromium catalyst was used, treated by the method of Maslyanskii and Rabinovich [10] for 4 hours at 550° with steam and then reduced at 375° with hydrogen for 2 hours. Each experiment was carried out on a fresh portion of catalyst; for this purpose the catalyst treated as described above was weighed out in 1-ml portions and stored until the experiment in sealed ampoules. The starting substances, purified from sulfur compounds, were distilled (except for *m*-cresol) on a rectification column with an efficiency of 80 theoretical plates. Their physical constants coincided with literature data.

The measurements were carried out in the range 360—400° at a component ratio water : hydrocarbon $\sim 20 : 1$.

Analysis of the liquid and gaseous reaction products, as well as of carbonaceous deposits on the catalyst, was carried out on the complex chromatographic apparatus described in work [19].

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