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M. G. GONIKBERG and LI GUAN-NYAN

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## Abstract

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M. G. GONIKBERG and LI GUAN-NYAN

# KINETICS OF THE HOMOGENEOUS DESTRUCTIVE HYDROGENATION OF TOLUENE AND ORTHO-CRESOL

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The kinetics of the homogeneous destructive hydrogenation of aromatic hydrocarbons (toluene, ethyl-, *n*-propyl- and *n*-butylbenzenes, and tetralin) in a flow system at temperatures of about 500° was studied by M. S. Nemtsov and coworkers ([1]). The authors came to the conclusion that, to a first approximation, the reaction rate is satisfactorily described by the equation for a bimolecular reaction between the hydrocarbon and hydrogen. Despite the fact that the values of the pre-exponential factor in the Arrhenius equation found from the experimental data proved to be considerably larger than those calculated from the theory of active collisions, Nemtsov considered the occurrence of the reaction by a radical-chain mechanism to be unlikely. Later, in studies from our laboratory ([2-4]), data were obtained testifying in favor of a radical-chain scheme for this process. This scheme includes the interaction of molecular hydrogen with radicals formed during the thermal decomposition of the aromatic compound, with the formation of atomic hydrogen; the latter, in turn, interacts with molecules of the starting compound, splitting off a substituent (an alkyl radical from alkylbenzenes, hydroxyl from phenol, etc.), while the radicals formed, reacting with molecular hydrogen, again generate atomic hydrogen. Along with this there occur diverse processes of recombination of radicals and their interaction with molecules of the initial, intermediate, and final products, which is reflected in the composition chiefly of the high-boiling fractions.

The scheme set forth for the mechanism of the process also determines the complexity of its kinetics. Thus, in a study by one of us with V. E. Nikitenkov ([2]), it was found that the rate of homogeneous destructive hydrogenation of toluene at 450-490° increases with increasing hydrogen concentration less than proportionally to the latter; the first order of the reaction with respect to toluene is likewise not observed. On the basis of the scheme of the mechanism of the process set forth in ([2]), it was to be expected that the expression for the reaction rate $w$ by means of the equation

$$w = kP^m_{C_6H_5CH_3}P^n_{H_2} \tag{1}$$

Fig. 1. Diagram of the flow apparatus.

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can in general have only an approximate character. In equation (1), the values of $m$ and $n$ must depend on the ratio of the rate constants of the individual stages of the reaction and, consequently, may change with temperature. According to ([2]), $m \geq 0.5$ and $n \leq 1$. Recently Silsby and Sawyer ([5]) reported that the rate of thermal demethylation of toluene in the presence of hydrogen at atmospheric pressure and at temperatures of 700-950° is proportional to the concentration of toluene and to the square root of the hydrogen concentration. Accepting, in the main, the scheme of the reaction mechanism proposed in ([2]), the authors considered it possible to neglect many reverse and "side"reactions, which enabled them to justify the indicated kinetic dependence.

Furthermore, in paper (5) the assumption was made that the concentration of atomic hydrogen in the reaction sphere during homogeneous destructive hydrogenation is determined by the dissociation equilibrium of molecular hydrogen. In a subsequent paper from the same laboratory (6), the kinetics of the same reaction were studied at a pressure of 100 atm and 540-660°. Under these conditions, the kinetic equation proposed earlier (5) proved no longer to be very satisfactory, and the rate constants found from it differed substantially from those calculated from the data of paper (5). The authors (6) suggested the possibility that the reaction mechanism changes with temperature.

The facts set forth prompted us to investigate the kinetics of homogeneous destructive hydrogenation of toluene at 530°—a temperature close to that used in papers (1,5)—in a flow system (the study (2) was carried out in an autoclave, which made it difficult to obtain accurate kinetic data). In the present work, homogeneous destructive hydrogenation of *ortho*-cresol was also investigated (previously studied by us under autoclave conditions (7)). The total pressure in the system ranged from 45 to 135 atm.

**Fig. 1.** Diagram of the flow apparatus.
**1** —measuring vessel; **2** —fine-control valve; **3** —sight window; **4** —reactor; **5** —reducing valve; **6** —rotameter; **7** —receiver; **8** —gas meter; **9** —porcelain; **10** —steel cylinder; **11** —thermocouple; **12** —reaction zone.

The scheme of the apparatus used by us is shown in Fig. 1. Toluene (or *o*-cresol), taken in an amount of 40 g, entered from measuring vessel **1** through fine-control valve **2** into reactor **4** (with an internal diameter of 30 mm). The rate of feed of the raw material was monitored by counting drops through sight window **3**, below which hydrogen was introduced into the reactor. The mixture of hydrogen and feedstock, after passing through a preheating layer of porcelain **9** (100 mm long), entered through a narrow annular gap (1 mm) between the reactor walls and steel cylinder **10** into the reaction zone (volume 125 ml), bounded below by a second cylinder **10**. In the reaction zone the temperature was kept constant

within $±$2°. The hydrogen flow rate was monitored with rotameter **6** and gas meter **8** after reducing valve **5**. The nominal contact time $\tau$ was calculated from the relation $\tau = V/v$, where $V$ is the volume of the reaction zone; $v$ is the volume of the mixture of vapors of the starting substance and hydrogen passing through the reaction zone per unit time.

Toluene and *o*-cresol were preliminarily distilled on a rectification column with an efficiency of 20 theoretical plates and were characterized by the following constants: toluene b.p. 110.4–110.6°/760, $n_D^{20}$ 1.4968; *o*-cresol b.p. 191.3–191.5°/760, $n_D^{20}$ 1.5454. The liquid reaction products were distilled on a column of the same efficiency. In experiments with toluene, the following were collected: a benzene fraction (b.p. 79.5–95°, $n_D^{20}$ from 1.5002 to 1.5005) and a toluene fraction (b.p. 95–110.6°, $n_D^{20}$ from 1.4966 to 1.4968). In experiments with cresol, the liquid reaction products, after drying, were separated into five fractions. Fraction 1 (up to 95°) contained predominantly benzene; about

95% of it had b.p. 75–82°, $n_D^{20}$ from 1.4875 to 1.4980. Fraction 2 (95–113°, $n_D^{20}$ 1.4950–1.4958) contained toluene. Fraction 3 (113–175°) was transitional. Fraction 4 (175–186.5°) contained phenol; fraction 5 (186.5–192°) was unchanged cresol. The residue after distillation contained about 75% cresol. For the composition of the reaction products boiling above *o*-cresol, as well as of the gaseous products, see (7).

Table 1 gives the results of experiments with toluene at 530°. To describe the kinetics of the process we used equation (1), in order to compare our data with the results of works (1) and (5, 6). The reaction order with respect to toluene, $m_T$, was found by us by fitting according to equation (2):

$$kP_{\mathrm{H2}} = kP_{\mathrm{H2}}^{n_T} = \frac{P_0^{1-m_T} - P^{1-m_T}}{(1-m_T)\tau(RT)^{1-m_T}} \left(\frac{\mathrm{mol}}{\mathrm{ml}}\right)^{1-m_T} \mathrm{h}^{-1}, \qquad (2)$$

where $P_0$ and $P$ are the initial and final partial pressures of toluene. The calculations were carried out from the data of experiments Nos. 1–7, in which the partial pressure of hydrogen was approximately the same (about 75 atm). The best constancy of the "constant" $kP_{\mathrm{H2}}$ was obtained at $m_T = 0.8$. The values of $kP_{\mathrm{H2}}$ calculated in this way are given in Table 1.

**Table 1**

**Homogeneous destructive hydrogenation of toluene at 530°**

Fig. 2. Determination of the reaction order with respect to hydrogen ($n_T$);

Figure 2: Fig. 2. Determination of the reaction order with respect to hydrogen ($n_T$);

| Experiment No. | $P_{total}$, atm | Partial pressures, atm: $C_7H_8$ | Partial pressures, atm: $H_2$ | $\tau$, h | Yield* of benzene in mol.% | $kP_{H2}$ at $m_T$ = 0.8 | Experiment No. | $P_{total}$, atm | Partial pressures, atm: $C_7H_8$ | Partial pressures, atm: $H_2$ | $\tau$, h | Yield* of benzene in mol.% | $kP_{H2}$ at $m_T$ = 0.8 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 90 | 16.2 | 73.8 | 0.420 | 13.4 | 0.594 | 9 | 75 | 25.7 | 49.3 | 0.480 | 10.8 | 0.448 |
| 2 | 90 | 16.7 | 73.3 | 0.505 | 17.0 | 0.634 | 10 | 45 | 16.4 | 28.6 | 0.411 | 5.9 | 0.249 |
| 3 | 100 | 25.0 | 75.0 | 0.608 | 18.0 | 0.633 | 11 | 60 | 16.0 | 44.0 | 0.417 | 9.1 | 0.373 |
| 4 | 100 | 26.3 | 73.7 | 0.775 | 21.7 | 0.591 | 12 | 75 | 15.7 | 59.3 | 0.409 | 12.4 | 0.525 |
| 5 | 100 | 27.2 | 72.8 | 0.500 | 15.8 | 0.627 | 13 | 105 | 15.4 | 89.6 | 0.418 | 16.3 | 0.673 |
| 6 | 100 | 24.9 | 75.1 | 0.202 | 6.1 | 0.605 | 14 | 120 | 15.7 | 104.3 | 0.421 | 19.4 | 0.795 |
| 7 | 105 | 31.0 | 74.0 | 0.505 | 14.3 | 0.595 | 15 | 120 | 15.9 | 104.1 | 0.535 | 21.7 | 0.745 |
| 8 | 100 | 30.2 | 69.8 | 0.296 | 9.6 | 0.667 | 16 | 135 | 16.1 | 118.9 | 0.424 | 20.1 | 1.005 |

* Allowing for 5% losses.

To determine the reaction order with respect to hydrogen ($n_T$), the data of experiments Nos. 1, 2 and 8-16 were plotted as $\lg kP_{H2}$, $\lg P_{H2}$ (see Fig. 2). The straight line obtained corresponds to a value of $n_T$ equal to 0.9. Thus, the kinetics of homogeneous destructive hydrogenation of toluene at 530° can be approximately described by the equation:

$$w = kP^{0.8}_{C_6H_5CH_3} P^{0.9}_{H2}. \quad (3)$$

It should be noted that treatment of the results of our experiments by the equation of a bimolecular reaction (1), and also by equation (1) with $m_T = 1.0$ and $n_T = 0.5$ (5, 6), did not lead to satisfactory results.

Results of analogous experiments with *o*-cresol at 550° are given in Table 2. The reproducibility of the results in these experiments proved not as good as in the experiments with toluene, which is explained by the necessity of drying the reaction product from the water formed, and also of allowing for the small amount of unchanged cresol in the high-boiling residue. Selection of the values of $m_{cr}$ according to equation (2) gave

**Fig. 2. Determination of the reaction order with respect to hydrogen ($n_T$);**

best results at $m_{cr} = 0.7$. From a graph analogous to Fig. 2, the reaction order

with respect to hydrogen was found; it proved to be close to 0.6 (according to experiments Nos. 20–25).

**Table 2**

**Homogeneous destructive hydrogenation of *o*-cresol at 550°**

| Experiment No. | $P_{tot}$, atm | Partial pressures, atm: *o*-cresol | Partial pressures, atm: $H_2$ | $\tau$, h | Composition of liquid products, wt.% relative to feed cresol*: benzene fr. 1 | Composition of liquid products, wt.% relative to feed cresol*: toluene fr. 2 | Composition of liquid products, wt.% relative to feed cresol*: phenol fr. 4 | Composition of liquid products, wt.% relative to feed cresol: *unchanged* o*-cresol** | $kP_{H_2}$ at $m_{cr}$ = 0.7 |
|---|---|---|---|---|---|---|---|---|---|
| 17 | 120 | 47.4 | 72.6 | 0.684 | 4.5 | 8.6 | 23.0 | 44.5 | 3.339 |
| 18 | 100 | 24.6 | 75.4 | 0.524 | 4.8 | 9.0 | 23.6 | 45.0 | 3.549 |
| 19 | 100 | 25.1 | 74.9 | 0.523 | 4.7 | 9.0 | 23.9 | 47.1 | 3.333 |
| 20 | 90 | 16.2 | 73.8 | 0.485 | 5.0 | 8.3 | 22.9 | 45.0 | 3.374 |
| 21 | 60 | 15.1 | 44.9 | 0.511 | 2.8 | 7.4 | 21.7 | 53.3 | 2.380 |
| 22 | 75 | 15.6 | 59.4 | 0.527 | 4.7 | 9.1 | 23.5 | 47.8 | 2.853 |
| 23 | 105 | 15.1 | 89.9 | 0.497 | 6.6 | 9.2 | 25.0 | 42.5 | 3.440 |
| 24 | 120 | 15.1 | 104.9 | 0.493 | 7.9 | 9.7 | 25.0 | 36.9 | 3.941 |
| 25 | 135 | 15.5 | 119.5 | 0.518 | 8.6 | 9.4 | 27.2 | 35.9 | 3.873 |

* The table does not include data on the transition fraction No. 3 (0.8–1.5 wt.%) and the residue, nor on the water content.
** Fraction 5 + 75% of the residue, which amounted to 5–8 wt.%.

Thus, the kinetics of homogeneous destructive hydrogenation of *o*-cresol at 550° is approximately described by the equation

$$w = kP^{0.7}_{CH_3C_6H_4OH}P^{0.6}_{H_2}. \quad (4)$$

The results presented above make it possible to conclude that neither the equation for a bimolecular reaction nor the equation proposed in works ([5,6]) is consistent with the experimental data obtained by us. Homogeneous destructive hydrogenation of aromatic hydrocarbons and their derivatives proceeds by a

complex radical-chain mechanism*; the rate of this process can be described only approximately by an equation of the form (1), in which the exponents of the concentrations of hydrogen and of the compound under study differ depending on the structure of this compound (possibly also on the temperature). The available data make it possible to suppose that the values of these exponents vary within the range from 0.5 to 1.0.

In conclusion, we note that carrying out the process of homogeneous destructive hydrogenation of *o*-cresol at temperatures higher than those used by us in the kinetic study leads to the production (along with benzene and toluene) of considerable yields of phenol at sufficiently high space velocities of cresol. Thus, for example, at 700°, a hydrogen partial pressure of 30 atm, $M_{H_2} : M_{\text{cresol}} = 3 : 1$, and a space velocity of 4.5 $h^{-1}$, we obtained 6.8 wt.% benzene, 10.4 wt.% toluene, and 26.2 wt.% phenol.

Institute of Organic Chemistry named after N. D. Zelinsky
Academy of Sciences of the USSR

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* We found that nitrogen oxide, added to hydrogen in an amount of 1%, somewhat inhibits the demethylation of toluene at 490° and 250 atm.

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