

## COMPETITIVE HYDROGENATION OF METHYLBENZENES ON A COBALT-MOLYBDENUM CATALYST

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Hydrogenation of benzene, toluene, xylenes and trimethylbenzenes and dehydrogenation of cyclohexane, methylcyclohexane, and 1,4-dimethylcyclohexane over a reduced Co-Mo-Al<sub>2</sub>O<sub>3</sub> catalyst was studied by the method of competitive reactions at 350°C and 0.5–2.0 MPa (5–20 atm). Hydrogenation competitive activity passes through maximum for toluene, while dehydrogenation activity monotonously increases with increasing molecular weight. Both trends are mutually confronted by means of equilibrium constant of given reactions. The adsorptivities of the hydrocarbons were compared by chromatographic adsorption measurements in hydrogen at 350°C on the reduced catalyst. Adsorption coefficients increase with molecular weight, which was compared with the known stability constants of some charge-transfer complexes. The relative reactivities in hydrogenation and relative adsorption coefficients were used to calculate relative rate constants of surface reaction which decrease with increasing molecular weight.

In connection with our interest in hydrogenation-dehydrogenation properties of a Co-Mo-Al<sub>2</sub>O<sub>3</sub> catalyst<sup>1</sup> and structure-reactivity relationships<sup>2–5</sup> we have examined competitive hydrogenation of methylbenzenes on the Co-Mo-Al<sub>2</sub>O<sub>3</sub> catalyst. The method of competitive reaction was used for this reaction also by other authors, however, under different conditions and with different catalysts (Pt (ref.<sup>6</sup>), Rh (ref.<sup>7</sup>), Ni (ref.<sup>8</sup>)).

We made use also of our experience from the study of other reactions by this method<sup>1,5,9</sup>.

Relative reactivities from competitive experiments are composed constants. We made an attempt to confirm their more general validity and physical meaning by comparing competitive hydrogenation of methylbenzenes and dehydrogenation of some methylcyclohexanes. Reactivities corresponding to pairs of substances for competitive hydrogenation and dehydrogenation ought to be interrelated through equilibrium constants of the reaction. Relative reactivities have physical meaning according to the suggested reaction scheme. In hydrogenation of aromatic hydrocarbons the scheme involves in general at least one equilibrium step, the adsorption of a hydrocarbon on a catalyst, preceding the rate-determining step. The reactivity thus comprises of the ratio of adsorption coefficients and the ratio of rate constants.

These ratios can sometimes be separated by kinetic experiments with single compounds<sup>6-8</sup>. We have obtained the ratio of adsorptivities chromatographically, directly at the reaction temperature 350°C. By using the same method, the adsorptivity of hydrocarbons, among others also of benzene and toluene, on the Co-Mo-Al<sub>2</sub>O<sub>3</sub> catalyst was followed already by Faschutbinov and coworkers<sup>10</sup>.

## EXPERIMENTAL

**Chemicals.** A Co-Mo-Al<sub>2</sub>O<sub>3</sub> catalyst G-35A (Girdler, FRG), was crushed to 0.25–0.5 mm particles for kinetic measurements and to 0.5–0.63 mm particles for adsorption measurements. Benzene, toluene, *m*-xylene, *p*-xylene (Lachema), *o*-xylene (Reachim), 1,3,5-trimethylbenzene, 1,2,4-trimethylbenzene (Fluka), 1,2,3-trimethylbenzene (Koch-Light), and cyclohexane (BDH) were commercial products and were used without further purification. Dimethylcyclohexanes and trimethylcyclohexanes (mixtures of *cis*- and *trans*-isomers) for dehydrogenation and calibration of a chromatograph were prepared by hydrogenation of corresponding aromatic hydrocarbons in a flow reactor at atmospheric pressure on platinum<sup>11</sup>; with 35 g of the catalyst (20% by weight of Pt on an active carbon) and at 150°C, a 0.75 mol h<sup>-1</sup> hydrogen flow rate and a 0.016 mol h<sup>-1</sup> feed of a hydrocarbon, the conversion was essentially 100% with all the hydrocarbons.

**Hydrogenation apparatus.** A flow tubular reactor was used. Hydrogen was taken from a pressure cylinder *via* a standard pressure reducing valve for air (the output to 2.5 MPa (25 atm)), the pressure after the condenser of the products was reduced by a standard valve for hydrogen and the flow rate was measured and controlled after this valve, *i.e.* at atmospheric pressure. Hydrogen was purified by passing over a deoxidation CHEROX 40-00 catalyst at 70°C and dried over a Calsit 5A molecular sieve. Liquid reactants were fed to an evaporator with a continual piston feeder. The reactor consisted of a stainless steel tube (14 mm i.d.) with centrally located thermocouple well. Product condenser which was cooled with a dry ice ethanol mixture was filled with a metallic netting and its contents were discharged by a capillary tube *via* a needle valve. Its efficiency was proved by blank experiments with mixtures of hydrocarbons.

**Procedure for kinetic measurements.** The catalyst was reduced at atmospheric pressure for 8 h at 450°C and then it was cooled to the reaction temperature 350°C. The pressure was 2.0 MPa (20 atm) for hydrogenation and 0.5 or 2.0 MPa (5 or 20 atm) for dehydrogenation. The reactor was fed with pairs of reactants. Their molar ratio in the feed  $\alpha$  was 0.3 to 3.0 for hydrogenation, the sum of their partial pressures  $\sum p_i = 0.015$  to 0.1 MPa (0.15 to 1 atm), the catalyst load  $W/F = 0.6$  to 0.8 kg<sub>cat</sub> h mol<sup>-1</sup> and the conversions attained 3–50%. For dehydrogenation:  $\alpha = 1.0$ ,  $\sum p_i = 0.05$  MPa,  $W/F = 0.6$ –0.8 and conversions 7–65%. The activity of the catalyst was constant. The extent of side reactions, which was followed also in experiments with single compounds, *i.e.* that of dealkylation and isomerisation, was 0–20% rel. of the total conversion.

**Analysis of products.** Mixtures were analysed by gas chromatography on a 1.5 m × 4 mm column filled with 10% poly(ethylene glycol adipate) on Rybosorb BLK 0.2–0.315 mm (Lachema). Hydrogen flow rate was 40 ml min<sup>-1</sup>, column temperature was 90–110°C in dependence on the analysed mixture; the apparatus was equipped with a thermal conductivity detector. The column separated partially *cis*, *trans*-isomers of di- and trimethylcyclohexanes. We assumed that these have the same response. As far as side products were identified, these were considered in calculating conversions.

*The apparatus and procedure for adsorption measurements.* Pulses of hydrocarbons were injected by microsyringe to a preheated stream of the gas ( $0.15$  to  $0.3 \text{ mol h}^{-1}$ ) at the inlet to a  $2.5 \text{ m} \times 4 \text{ mm}$  stainless steel column. Pressure drop on the column was  $20$ – $60 \text{ kPa}$  ( $0.2$ – $0.6 \text{ atm}$ ). The outlet of the column was connected to a thermal conductivity detector. Hydrocarbons could be fed also continuously, by a linear feeder. The catalyst ( $25 \text{ g}$ ) was reduced in the column at  $450^\circ\text{C}$  for  $4 \text{ h}$ . Before commencing adsorption measurements  $1,3,5$ -trimethylbenzene ( $F = 0.1 \text{ mol h}^{-1}$  of the hydrocarbon,  $0.4 \text{ mol h}^{-1}$  of  $\text{H}_2$ ,  $350^\circ\text{C}$ ) was continuously introduced over the catalyst for  $0.5 \text{ h}$ . Pulses of the reactants were  $40 \mu\text{l}$ . Retention times were read from peak maxima and an allowance was made for the retention time of the inert, which in our case was nitrogen.

## RESULTS AND DISCUSSION

Competitive hydrogenation experiments were treated similarly as in our previous works concerned with other reactions<sup>1,5,9</sup>. The molar ratio of reactants in the feed  $\alpha$  was changed from  $0.3$  to  $3.0$  for benzene/toluene and toluene/*o*-xylene pairs. Obtained conversions  $x_i$ , about  $15$  values for each pair, confirmed that the partial pressure of aromatic hydrocarbon in the numerator of the kinetic equation is in the first power<sup>9</sup>. For other pairs we obtained only  $3$ – $8$  pairs of conversions at  $\alpha = 1$ . Relative reactivities  $R$  were determined as the slopes of the dependence  $x_1 = h(x_2)$

TABLE I  
Relative Reactivities

Pairs	$R$ or $R'$
Hydrogenation <sup>a</sup>	
Toluene/benzene	1.6
Benzene/ <i>o</i> -xylene	1.5
Benzene/ <i>m</i> -xylene	1.1
Benzene/ <i>p</i> -xylene	1.7
Toluene/ <i>o</i> -xylene	1.8
Toluene/ <i>m</i> -xylene	2.1
Toluene/ <i>p</i> -xylene	1.7
Toluene/1,2,3-trimethylbenzene	2.3
Toluene/1,2,4-trimethylbenzene	7.0
Toluene/1,3,5-trimethylbenzene	8.0
Dehydrogenation	
Methylcyclohexane/cyclohexane	3.0 <sup>b</sup>
1,4-Dimethylcyclohexane/cyclohexane	2.0 <sup>a</sup>

<sup>a</sup>  $350^\circ\text{C}$ ,  $2 \text{ MPa}$  ( $20 \text{ atm}$ ); <sup>b</sup>  $350^\circ\text{C}$ ,  $0.5 \text{ MPa}$  ( $5 \text{ atm}$ ).

in the origin and are presented in Table I. From these values we calculated relative reactivities with respect to benzene  $R_{\text{rel}}$  (e.g.<sup>8</sup>) which are listed in Table II. The reactivity passes through maximum for toluene. The fact that under our conditions toluene is more reactive than benzene follows also independently from the pairs of reactivities of benzene and toluene with respect to individual xylenes. An indication of such a maximum was observed by Ziuba and Krichko<sup>12</sup> on a sulphurized Co-Mo-Al<sub>2</sub>O<sub>3</sub> catalyst. The authors found the following reactivity order; benzene < toluene  $\simeq$   $m$ -xylene. To confirm the existence of this maximum and physical meaning of reactivities we have performed also competitive dehydrogenation of the pairs cyclohexane/methylcyclohexane and methylcyclohexane/1,4-dimethylcyclohexane. A mutual interrelation between competitive hydrogenation and dehydrogenation of corresponding substances can be made clear from a simple Langmuir-Hinshelwood kinetic model for parallel reactions (A) and (B).

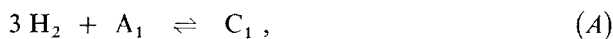


TABLE II

Relative Reactivities with Respect to Benzene and Cyclohexane

Reactant	$R_{\text{rel}}$ or $R'_{\text{rel}}$
Hydrogenation	
Benzene	1.0
Toluene	1.6
<i>o</i> -Xylene	0.7
<i>m</i> -Xylene	0.9
<i>p</i> -Xylene	0.6
1,2,3-Trimethylbenzene	0.7
1,2,4-Trimethylbenzene	0.2
1,3,5-Trimethylbenzene	0.2
Dehydrogenation	
Cyclohexane	1.0
Methylcyclohexane	3.0
1,4-Dimethylcyclohexane	6.0

The rate  $r_i$  for each reaction can be written as

$$r_i = \frac{k_{A_i} K_{A_i} p_{A_i} f(p_H) - k_{C_i} K_{C_i} p_{C_i}}{g(p_H, p_{A_1}, p_{A_2}, p_{C_1}, p_{C_2})} \quad (1)$$

where  $A_i$  and  $C_i$  denote an aromatic hydrocarbon and the corresponding cyclohexane,  $H$  is hydrogen,  $k_{A_i}$  is the rate constant for hydrogenation,  $k_{C_i}$  that for dehydrogenation,  $K_{A_i}$  and  $K_{C_i}$  are adsorption constants,  $p$  is partial pressure and  $f(p)$ ,  $g(p)$  are partial pressure functions of usual type. By dividing the rates  $r_1$  and  $r_2$  and by transformation we obtain

$$\frac{dx_1}{dx_2} = \frac{k_{A_1} K_{A_1} f(p_H) (1 - x_1) - k_{C_1} K_{C_1} x_1}{k_{A_2} K_{A_2} f(p_H) (1 - x_2) - k_{C_2} K_{C_2} x_2} \quad (2)$$

where  $x_i = p_{C_i} / (p_{A_i} + p_{C_i})$ . The course of the dependence  $x_1 = h(x_2)$  is shown in Fig. 1. If the equilibrium is such, or conversions are small enough, that the reverse reaction can be neglected, than for hydrogenation it holds that

$$R = \frac{\log(1 - x_1)}{\log(1 - x_2)} = \frac{k_{A_1} K_{A_1}}{k_{A_2} K_{A_2}} \quad (3)$$

Similarly, for dehydrogenation and with analogous presumptions one can write

$$R' = \frac{\log(x_1)}{\log(x_2)} = \frac{k_{C_1} K_{C_1}}{k_{C_2} K_{C_2}} \quad (4)$$

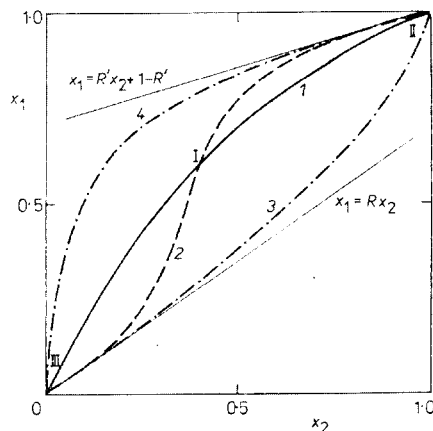


FIG. 1

Schematic Course of Dependences  $x_1 = f(x_2)$  for Reversible Competitive Reactions

1 Mutual dependence of equilibrium conversions; 2, 3, 4 the course of the dependence providing that equilibrium corresponds to points I, II, and III, respectively.

Since in the equilibrium  $r_i = 0$ , then

$$\mathcal{K}_1 \frac{(p_H)^3}{f(p_H)} = \frac{k_{A1}K_{A1}}{k_{C1}K_{C1}}, \quad (5)$$

$$\mathcal{K}_2 \frac{(p_H)^3}{f(p_H)} = \frac{k_{A2}K_{A2}}{k_{C2}K_{C2}}, \quad (6)$$

where  $\mathcal{K}_i$  are equilibrium constants of hydrogenation of reactant  $A_i$ . Combination of Eqs (3) to (6) yields

$$R/R' = \mathcal{K}_1/\mathcal{K}_2 = \mathcal{K}_{rel}. \quad (7)$$

The same relation can be derived also for other than Langmuir–Hinshelwood kinetics. Relative reactivities are only formed by other constants, for example, only by rate constants of consecutive steps, and the relation may be valid with some limitations, *e.g.* at a constant hydrogen pressure.

Relative reactivities for dehydrogenation  $R'$ , obtained each as the slope to the curve  $x_1 = h(x_2)$  from the five pairs of conversions in the point  $x_1 = x_2 = 1$ , are presented in Table I and the reactivities calculated from them with respect to cyclo-

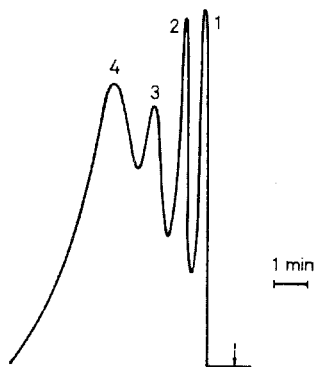


FIG. 2

Separation of Hydrocarbons on a Co–Mo– $\text{Al}_2\text{O}_3$  Catalyst Atmospheric pressure  $350^\circ\text{C}$ , nitrogen as a carrier gas  $0.2 \text{ mol h}^{-1}$ , pressure drop on the column was 60 kPa, 0.1 ml of the mixture.

1. Benzene, 2 toluene, 3 *m*-xylene, 4 1,3,5-trimethylbenzene.

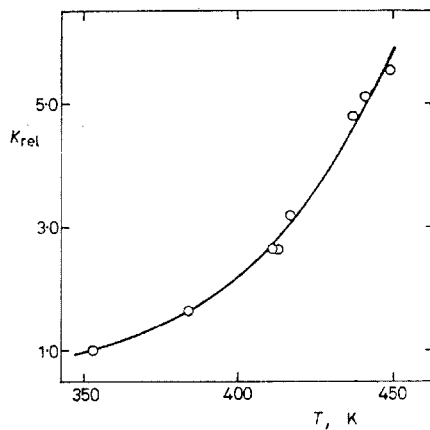


FIG. 3

Correlation of Adsorption Coefficient with Boiling Point

hexane,  $R'_{rel}$ , are summarized in Table II. The ratio of equilibrium constants of hydrogenation of toluene and *p*-xylene with respect to benzene  $\mathcal{K}_{rel}$  were obtained by comparing data reported by Vvedenskii<sup>13</sup> (only benzene and toluene) and Stull and co-workers<sup>14</sup>. These were very similar according to both sources and that for benzene 1.0 (by definition), toluene 0.4, and *p*-xylene 0.1. As  $R'_{rel}$  monotonously increases in the series cyclohexane, methylcyclohexane, 1,4-dimethylcyclohexane and relative equilibrium constants  $\mathcal{K}_{rel}$  monotonously decrease, according to Eq. (7) it is possible that  $R_{rel}$  would pass through a maximum. In fact, the following values were obtained from  $R'_{rel}$  and  $\mathcal{K}_{rel}$  using Eq. (7): benzene 1.0, toluene 1.4, and *p*-xylene 0.6.

The character of the separation of substances in adsorption experiments, which is similar in both nitrogen and hydrogen, is seen in Fig. 2. In hydrogen, the reaction does not take place, since at atmospheric pressure the equilibrium is shifted to the side of aromatic hydrocarbon. Relative adsorption coefficients in hydrogen with respect to benzene  $K_{rel}$  are listed in Table III and their correlation with boiling points of hydrocarbons is graphically represented in Fig. 3. Adsorption coefficient of a hydrocarbon increases with its molecular weight. Also Faschutbinov and co-workers<sup>10</sup> observed in similar experiments at 150–300°C that toluene adsorbs twice as strongly as benzene. The same trend found for the coefficients (under other conditions and on other metals) determined kinetically, *i.e.* by combination of simple and competition reactions<sup>6,8</sup>, gravimetrically<sup>15</sup> or by IR spectroscopy<sup>16</sup>. It is assumed that  $\pi$  electrons play a role during adsorption of a hydrocarbon and that the stability of surface complexes parallels *e.g.* the stability of the so-called charge-transfer complexes. Völter and coworkers<sup>15</sup> compared *e.g.* the adsorption coefficients obtained

TABLE III  
Relative Equilibrium Constants of Formation of Complexes and Hydrogenation Parameters

Hydrocarbon	Complexes			Hydrogenation	
	HCl <sup>a</sup>	TCNE <sup>b</sup>	HgCl <sub>2</sub> <sup>c</sup>	$K_{rel}$ <sup>d</sup>	$k_{rel}$
Benzene	1.00	1.00	1.00	1.00	1.00
Toluene	1.51	1.85	1.39	1.64	0.98
<i>o</i> -Xylene	1.85	3.49	1.64	3.18	0.21
<i>m</i> -Xylene	2.07	3.00	—	2.64	0.34
<i>p</i> -Xylene	1.64	3.82	—	2.64	0.25
1,2,3-Trimethylbenzene	2.39	—	—	6.09	0.1
1,2,4-Trimethylbenzene	2.23	—	—	5.27	0.05
1,3,5-Trimethylbenzene	2.61	8.65	2.14	4.64	0.05

<sup>a</sup> Ref.<sup>17</sup>; <sup>b</sup> tetracyanoethylene, ref.<sup>18</sup>; <sup>c</sup> ref.<sup>19</sup>; <sup>d</sup> 350°C, 100 kPa (1 atm), hydrogen as a carrier gas 0.26 mol g<sup>-1</sup>, pressure drop on a column was 50 kPa (0.5 atm).

gravimetrically with the stability of complexes of aromatic hydrocarbons with picric acid and ICl. In Table III are given equilibrium constants of some other complexes. The trend with molecular weight is unambiguous but the sequence of positional isomers is different for different acceptors and the same holds also for adsorption coefficients on various metals. This is likely due to a different operation of steric and electronic factors for different acceptors. A decrease in adsorption coefficients was observed only by Smith and Campbell<sup>7</sup> on nickel. This decrease was ascribed to steric effect of substituents.

From relative adsorption coefficients, reactivities and the relation (3) we determined relative rate constants  $k_{rel}$  (Table III) which decrease with increasing molecular weight. This agrees with the reactivity order found for isolated reactions (where the surface is extensively occupied and the reactivity is parallel to the rate constant of surface reaction) by Ziuba and Krichko<sup>12</sup> on a sulphurized Co—Mo—Al<sub>2</sub>O<sub>3</sub> catalyst at 4 MPa and 350°C, *i.e.* benzene > toluene > *m*-xylene. Such a decrease in rate constants was observed also under other conditions with other catalysts<sup>6-8,15</sup>. Interpretation of this phenomenon is not simple. It is not quite clear whether adsorption is followed directly by rate-determining step or by another equilibrium step *e.g.* by equilibrium between  $\pi$  and  $\sigma$  complexes<sup>15</sup>.

It becomes evident that an increase in adsorption coefficients and a decrease in rate constants with increasing molecular weight does not depend on a given catalyst and conditions and has more general character. Combination of both constants, *i.e.* the relative reactivity in competitive experiments, may, depending upon the magnitude of constants and their sensitivity to structural changes (which both vary from catalyst to catalyst) either decrease or increase monotonously with molecular weight, or it may, as in our case, pass through a maximum.

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