KINETICS OF COMPLEX HETEROGENEOUS CATALYTIC REACTIONS. VI.*

COMPETITIVE HYDROGENATION OF *o*-ALKYLPHENOLS ON A NICKEL CATALYST

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The reactivity of six *o*-alkylphenols in their hydrogenation on a nickel catalyst containing aluminium oxide was studied at 160°C in gaseous phase. Both initial rates of the hydrogenation of individual compounds and, by the method of competitive reactions, their relative reactivities with respect to phenol were measured. It has been qualitatively estimated that alkyl-substituted phenols adsorb weaker than phenol. Initial and competitive data were confronted with the results of separate kinetic analysis of the hydrogenation of phenol, which made it possible to separate the values of rate constants and adsorption coefficients for three alkylphenols. In an attempt to correlate these data with polar and steric constants of substituents it was observed that, with the exception of the methyl derivative, Taft equation can be used for estimating structure effects.

In a previous work[1] we studied the effect of structure of *o*-alkylphenols on their reactivity in hydrogenolytic dealkylation on a nickel catalyst containing aluminium oxide at 350°C. As this reaction is at lower temperatures accompanied by hydrogenation of the aromatic nucleus, the aim of the present work was to examine the reactivity of a series of *o*-alkylphenols in their hydrogenation on the same catalyst, and in the same experimental arrangement[1], at the temperature of 160°C.

In the preceding study[2] we made analysis of the use of the method of competitive reactions for determining relative reactivities in heterogeneous catalytic reactions. We have found that also in these cases relative reactivities can be reliably expressed, here as the product of relative rate constant and relative adsorption coefficient. From these quantities individual rate constants and adsorption coefficients can be obtained if the absolute values for a reference compound and several values of initial reaction rates for each of studied compounds are known. Both the procedures were used also in the present work.

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EXPERIMENTAL

Compounds Used

o-Cresol (Lachema, Brno), *o*-isopropylphenol (Koch-Light), *o*-sec-butylphenol (Koch-Light) and *o*-tert-butylphenol (Fluka) were commercial products. *o*-Ethylphenol and *o*-propylphenol were prepared in this laboratory within the framework of other studies[3,4]. All the alkylphenols were distilled at atmospheric pressure prior to use, and their purity was checked by chromatographic analysis. Phenol (Severomoravské chemické závody) was purified by fractional distillation on a 36 TP column. Electrolytic hydrogen (Elektrochemische Werke, Bitterfeld) and nitrogen for bulbs (Technoplyn, Ostrava), from pressure cylinders, were freed from traces of oxygen by passing over a palladium catalyst and dried by sodium hydroxide. The Ni-Al_2O_3 catalyst was prepared by co-precipitation of a mixture of the nitrates by potassium hydroxide. The weight ratio of Al_2O_3 to Ni was 8·4 : 91·6. The catalyst used throughout this study was from the same batch as that used in the previous work[1], and for each determination of conversion the reactor was charged with fresh portion of the catalyst, which was reduced by a stream of hydrogen directly in the reactor at 350°C over a period of 2 h.

Apparatus and Procedure

The flow apparatus with reactants in gaseous phase and procedure were similar to those used in our previous studies[5,6]. The hypodermic syringe, used to charge the reactants, was in the case of solid alkylphenols provided with a heating mantel and heated above the temperature of their melting point. The catalyst was mixed with glass balls to ensure uniform temperature distribution in the bed. Owing to very small amount of the catalyst (15—200 mg) used in the measurements and low conversions obtained, it was possible to maintain the bed temperature at 160°C within ±0·5°C by means of a temperature-controlled silicon oil bath. Preliminary experiments showed that in the used experimental region and for the chosen granulation of the catalyst (0·4—0·7 mm) neither external nor internal diffusion exerts any effect on the course of the reaction. The values of initial reaction rates were obtained graphically as the slope of the experimental dependence of the conversion x on the reciprocal space rate W/F at the point $W/F = 0$; up to $x = 0{\cdot}12$ this dependence was linear for all the compounds studied.

Analytical Methods

Each determination of conversion was made with three samples which were gradually taken after the steady state in the reactor had been established and analysed by gas chromatography. When studying the kinetics of hydrogenation of phenol, the reaction products were analysed on an instrument (Vývojové dílny ČSAV) equipped with thermal-conductivity detector, using a 2 m-column filled with 10 w. % dinonyl sebacate on Cellite 545 (180°C oven temperature, hydrogen as carrier gas). The analysis consisted of determination of the amounts of phenol and hydrogenation products (the sum of cyclohexanone and cyclohexanol). The analysis of the products of hydrogenation of other alkylphenols or of the competitive hydrogenation of their mixtures with phenol was made on Shandon chromatograph equipped with flame-ionisation detector, using a 2-m column filled with 30 w. % Apiezon on Cellite 545 (170°C oven temperature, hydrogen as carrier gas). In the analysis of the products of the hydrogenation of ethylphenol and higher alkylphenols at the conditions specified above the corresponding alkylcyclohexanols were separated from alkylcyclohexanones. In the case of the products of hydrogenation of binary mixtures, containing 6 substances, their separation was so satisfactory that conversions of both concurrent reactions could be independently determined.

RESULTS AND DISCUSSION

Kinetics of Hydrogenation of Phenol

A detailed kinetic study of the hydrogenation of the reference compound, phenol, was carried out by the method of initial reaction rates at the conditions which ensure practical irreversibility of the reaction (160°C). As it has been found by a number of authors that hydrogenation of phenols is consecutive process leading *via* corresponding cyclohexanone to cyclohexanol[7-11], it was possible to express phenol conversion as the sum of the formation of cyclohexanone and cyclohexanol. We have determined 20 values of initial reaction rates at the four values of the sum of partial pressures of phenol and hydrogen ($p_F^0 + p_B^0$) equaling to 0·25; 0·5; 0·75 and 1 atm (the pressure was reduced by diluting the mixture of reactants with nitrogen). For each of these values five different ratios of hydrogen to phenol were used; the partial pressure of phenol varied within 0·03–0·45 atm, and that of hydrogen within 0·08–0·95 atm. The higher partial pressures of phenol were not used because of the danger of its condensation in the reactor.

TABLE I

Types of Rate Equations Used to Description of Initial Rate of Hydrogenation of Phenol

The values b equal to 1 or 0·5, depending upon whether adsorption of hydrogen is assumed to take place without or with dissociation. The rate-controlling step is: ads F adsorption of phenol, ads B adsorption of hydrogen, sr F2B surface reaction of phenol with two molecules of hydrogen (Scheme (*A*)), sr FB surface reaction of phenol with one molecule of hydrogen (the first step in Scheme (*B*)), sr F1/2B surface reaction of phenol with one hydrogen atom, des R desorption of reaction product.

Eq. type	Right-hand side of rate equation $r_F^0 = f(p_F^0, p_B^0)$	Rate-controlling step	s	Note
(*1*)	$k_{ads}p_F^0/[1 + (K_Bp_B^0)^b]^s$	ads F	1, 2	
(*2*)	$k_{ads}p_B^0/[1 + K_Fp_F^0]^s$	ads B	1, 2	
(*3*)	$kK_Fp_F^0p_B^{02}/[1 + K_Fp_F^0]^s$	sr F 2 B	1, 2	B is not adsorbed
(*4*)	$kK_Fp_F^0(K_Bp_B^0)^2/[1 + K_Fp_F^0 + (K_Bp_B^0)^b]^s$	sr F 2 B	3, 5	
(*5*)	$kK_Fp_F^0p_B^0/[1 + K_Fp_F^0]^s$	sr FB	1–4	B is not adsorbed
(*6*)	$kK_Fp_F^0K_Bp_B^0/[1 + K_Fp_F^0 + (K_Bp_B^0)^b]^s$	sr FB	2–4	
(*7*)	$kK_Bp_F^0p_B^0/[1 + (K_Bp_B^0)^b]^s$	sr FB	1–3	A is not adsorbed
(*8*)	$kK_Fp_F^0(K_Bp_B^0)^{1/2}/[1 + K_Fp_F^0 + (K_Bp_B^0)^{1/2}]^2$	sr F 1/2 B	2	
(*9*)	$k_{des}K'K_Fp_F^0p_B^{02}/[1 + K_Fp_F^0 + K'K_Fp_F^0p_B^{02}]$	des R	1	B is not adsorbed
(*10*)	$k_{des}K'K_Fp_F^0(K_Bp_B^0)^2/[1 + K_Fp_F^0 + (K_Bp_B^0)^b + K'K_Fp_F^0(K_Bp_B^0)^2]$	des R	1	
(*11*)	$k(p_F^0)^\alpha(p_B^0)^\beta$	—	—	empirical power law equation

The obtained rate data were treated statistically by the combined method of linear and nonlinear regression[11]. 29 rate equations of the types presented in Table I were used. Similarly as in the previous work[11] we have presumed that transformation of phenol to cyclohexanone can proceed according to one of the two schemes,

$$\mathrm{F} + 2\,\mathrm{B} \rightarrow \mathrm{R} \qquad (A)$$

$$\mathrm{F} + \mathrm{B} \rightarrow \mathrm{M}, \quad \mathrm{M} + \mathrm{B} \rightarrow \mathrm{R} \qquad (B)$$

i.e. by simultaneous or subsequent addition of two molecules of hydrogen. In deriving the rate equations on the basis of Langmuir–Hinshelwood ideas we have made assumption that the rate controling steps could be adsorption of some of the starting compounds (relations of types (*1*) and (*2*)), surface reaction (*A*) (relations of types (*3*) and (*4*)), the first step of surface reaction (*B*) (relations of types (*5*)–(*7*)), or desorption of a product (relations of types (*9*) and (*10*)). The second step of surface reaction (*B*) was taken as fast since it represents the hydrogenation of very labile intermediate of cyclohexadiene type. We have also assumed that the rate of surface reaction could be controlled by surface reaction of adsorbed phenol with one hydrogen atom formed by dissociative adsorption of molecular hydrogen (relations of type (*8*)). It was further assumed that the reactants either adsorb without dissociation (hydrogen also with dissociation) or one of the reactants does not adsorb and reacts directly from gaseous phase (relations of types (*3*), (*5*), (*7*) and (*9*)). For the sake of comparison, experimental data were also treated with the use of empirical power law equation (*11*).

Some of these models turned out to be improbable (Eqs (*1*)–(*3*), (*7*) and (*8*)) already on treatment of data by linear regression, although very low value of the

TABLE II

Survey of Kinetic Models Treated by Non-Linear Regression

Order	Equation type	Rate-controlling step[a]	Range of Q
1	(*4*)	sr F 2 B	5 947– 6 969
2	(*6*)	sr FB	6 799– 7 681
3	(*5*)	sr FB	9 537–11 973
4	(*11*)	power law equation	12 922
5	(*9*)	des R	16 514

[a] See notes in Table I.

squared correlation coefficient was taken as the criterion ($\varrho^2 = 0{\cdot}5$). The other models were then treated by non-linear regression. We have found that experimental data are best described by the models of type (*4*) (Table II), of which the least sum of the squared deviations of the experimental from the calculated reaction rate ($Q = 5\,947$) was obtained with Eq. (*4a*)

$$r_F^0 = k_F K_F p_F^0 (K_B p_B^0)^2 / [1 + K_F p_F^0 + (K_B p_B^0)^{0{\cdot}5}]^5 \qquad (4a)$$

with optimum values of the constants $k_F = 14\,028$ mol kg^{-1} h^{-1}, $K_F = 2{\cdot}6$ atm^{-1}, and $K_B = 4{\cdot}9$ atm^{-1}. This model corresponds to the assumption that rate determining step involves surface reaction of the phenol with two hydrogen molecules adsorbed with dissociation (*A*). When compared with the model obtained by Hančil in the hydrogenation of phenol on platinum[11], the only difference can be seen in that on platinum the assumption of the adsorption of hydrogen without dissociation leads to better agreement with experimental data. Also other models in Table II (types (*6*) and (*5*)) even though worse than the models of type (*4*), presume that surface reaction of the adsorbed phenol, here, of course, only with one hydrogen molecule, is rate controlling. Very poor results were obtained with the use of power-law equation (*11*). The worst were relations of type (*9*), derived under assumption that desorption is rate controlling step. Equations of type (*10*), obtained under the same assumption, were not treated by non-linear regression, because they contained the greater number of parameters than was that for which the program at our disposal was designed. After all, on treatment by linear regression these equations gave lower values of the squared correlation coefficient ($\varrho^2 = 0{\cdot}87$) than did the equations of type (*4*) ($\varrho^2 = 0{\cdot}96$), although they contained one parameter more.

Without being inclined to draw detailed conclusions on reaction mechanism from the form of Eq. (*4a*), we believe that it fits experimental data with such an accuracy that on its basis the reactivity of individual alkylphenols can be compared.

Initial Rates of Hydrogenation of o-*Alkylphenols*

With the aim to compare reactivities of individual *o*-alkylphenols we first measured initial reaction rates of their hydrogenation at 160°C and partial pressure 0·05 atm; the hydrogen partial pressure was 0·95 atm. The values of initial reaction rates (Table III) do not satisfactorily correlate either with Taft polar constants of alkylsubstituents[12] or with steric constants[12]. This may be due to the fact that the values of reaction rates are function of the partial pressure used and further that they include both rate constants, and, in a relatively complex function, also adsorption coefficients, which may depend on the structure of a reactant in different way. The experimental values allow only to compare the order of hydrogenation reactivities with that of dealkylation reactivities[1]. As follows from Table III the reactivity order for hydrogenation differs significantly from that for dealkylation.

Competitive Hydrogenation of Alkylphenols

In order to evaluate relative reactivities of alkylphenols by means of a quantity which would not be dependent on partial pressures of reactants, we have used the method of competitive reactions[2,13-17]. A mixture of an alkylphenol with phenol was introduced into the reactor in the molar ratio 1 : 1, the partial pressure of the mixture being 0·05 atm and that of hydrogen 0·95 atm. The values of conversions, obtained at several reciprocal space velocities, were treated with the use of the

TABLE III

Initial Reaction Rates r_A^0 and Relative Reactivities R_A in Hydrogenation of Phenol and *o*-Alkylphenols at 160°C and p_A^0 (resp. $p_A^0 + p_F^0$) = 0·05 atm, p_B^0 = 0·95 atm

Substance A	r_A^0 mol h^{-1} kg^{-1}	r_A^0/r_F^0	Reactivity order in		R_A
			hydrogenation	dealkylation[1]	
Phenol	115	1	—	—	1
o-Cresol	54	0·47	4	1	0·23
o-Ethylphenol	77	0·67	2	2	0·305
o-Propylphenol	67	0·58	3	3	0·36
o-Isopropylphenol	37	0·32	5	4—5	0·20
o-Sec-butylphenol	32	0·28	6	4—5	0·115
o-Tert-butylphenol	113	0·98	1	6	0·39

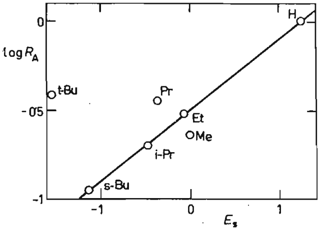

FIG. 1

Dependence of Logarithm of Relative Reactivity R_A on Steric Substituent Constants E_s

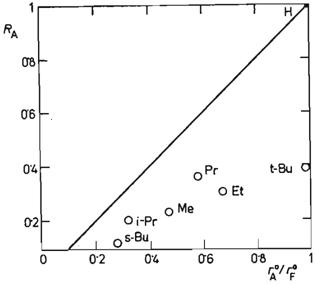

FIG. 2

Relationship between Relative Reactivities R_A and Relative Values of Initial Reaction Rates r_A^0/r_F^0

Eq.[2] (*12*)

$$R_A = k_A K_A / k_F K_F = \log(1 - x_A)/\log(1 - x_F)\,. \tag{12}$$

The mean values of the so obtained relative reactivities R_A are presented in Table III. We have made an attempt to correlate these values by Taft equation with structure effects[12]. Correlation of the reactivities with inductive substituent constants σ^* has failed. A certain correlation can be however observed with steric substituent constants E_S (Fig. 1), tert-butylphenol being, of course, out of the correlation. Fig. 2 shows a relation between the relative reactivities R_A from competitive reactions and the relative values of initial reaction rates, with respect to phenol. The values of relative reactivities R_A are always lower than those of relative reaction rates. It means that all the substituted phenols adsorb weaker than the unsubstituted derivative. From the ratio of intial reaction rates of the hydrogenation of phenol and an alkylphenol, expressed by Eq. (*4a*)

$$\frac{r_A^0}{r_F^0} = \frac{k_A K_A p_A^0 (K_B p_B^0)^2 / [1 + K_A p_A^0 + (K_B p_B^0)^{0 \cdot 5}]^5}{k_F K_F p_F^0 (K_B p_B^0)^2 / [1 + K_F p_F^0 + (K_B p_B^0)^{0 \cdot 5}]^5}\,, \tag{13}$$

we obtain the relation between R_A and (r_A^0/r_F^0),

$$R_A = \frac{r_A^0}{r_F^0}\,\frac{p_F^0}{p_A^0}\left(\frac{C + K_A p_A^0}{C + K_F p_F^0}\right)^5, \tag{14}$$

which is a linear relationship with the slope $Y = (p_F^0/p_A^0)\,[(C + K_A p_A^0)/(C + K_F p_F^0)]^5$. As p_A^0 and p_F^0 were the same and, as follows from Fig. 2, $R_A < (r_A^0/r_F^0)$, Y is lower than 1, and thus in all cases K_A is smaller than K_F. A weaker adsorption of substituted phenols may be due to steric hinderance by the alkyl group. The numerical values of K_A cannot be determined from the above r^0 data, because the partial pressure

TABLE IV

Values of Rate Constants k_A and Adsorption Coefficients K_A of Phenol, *o*-Cresol, *o*-Ethylphenol, and *o*-Isopropylphenol at 160°C

Compound	k_A mol h^{-1} kg^{-1}	k_A^{rel}	K_A atm^{-1}	K_A^{rel}
Phenol	14 028	1	2·6	1
o-Cresol	4 140	0·295	2·05	0·79
o-Ethylphenol	6 850	0·488	1·6	0·615
o-Isopropylphenol	6 070	0·433	1·2	0·46

used ($p_{\mathrm{A}}^0 = 0{\cdot}05$ atm) was low and, therefore, the effect of the term $K_{\mathrm{A}}p_{\mathrm{A}}^0$ so weakened that the calculation would be quite unreliable. It would be more relevant to measure reaction rates at a higher partial pressure of alkylphenols. This was not possible, however, because of high boiling points, and thus low vapour tension at the reaction temperature. Only with three alkylphenols (methyl-, ethyl-, and isopropyl-) did we carry out the measurements at a higher partial pressure.

With *o*-cresol and *o*-ethylphenol, we measured initial reaction rate also at $p_{\mathrm{A}}^0 = 0{\cdot}2$ atm, with *o*-isopropylphenol at $p_{\mathrm{A}}^0 = 0{\cdot}15$ atm. The rates were 57·9, 86·5, and 55·0 mol h^{-1} kg^{-1}, respectively. The adsorption coefficient K_{A} was obtained with the use of Eq. (*4a*). Its modification, performed similarly as in the previous work[2], leads to Eq. (*15*) (after substitution of index A for F)

$$K_{\mathrm{A}} = (1/p_{\mathrm{A}}^0)\,\{[Mp_{\mathrm{A}}^0(K_{\mathrm{B}}p_{\mathrm{B}}^0)^2/r_{\mathrm{A}}^0]^{1/5} - (K_{\mathrm{B}}p_{\mathrm{B}}^0)^{1/2} - 1\}\,, \tag{15}$$

where $M = k_{\mathrm{A}}K_{\mathrm{A}} = R_{\mathrm{A}}k_{\mathrm{F}}K_{\mathrm{F}}$. After substitution of these values together with the value of K_{B}, corresponding partial pressures and initial reaction rates, we calculated the values of adsorption coefficients K_{A} and, from the relation $k_{\mathrm{A}} = M/K_{\mathrm{A}}$, the values of rate constants. These are given in Table IV, along with the corresponding values for phenol. Although these values (except those for phenol) may be ladden with quite a great error, it can be seen that they decrease with increasing length of the alkyl substituent. The only substituent which deviates from the correlations of rate constants and adsorption coefficients with polar and steric constant of substituents by means of Taft equation is the methyl substituent (*o*-cresol). A similar behaviour of the methyl group has also been observed in the dealkylation of alkylbenzenes on a nickel–aluminium oxide catalyst[18]. The reason of this behaviour is still uncertain.

LIST OF SYMBOLS

b	exponent of the adsorption term of hydrogen in the denominator of rate equations, equaling to 1 or 0·5 in dependence on whether hydrogen is assumed to be adsorbed without or with dissociation
C	constant in Eqs (*13*) and (*14*), equaling to $1 + (K_{\mathrm{B}}^0 p_{\mathrm{B}}^0)^{0{\cdot}5}$
E_{s}	steric substituent constant[12]
F	feed rate (mol h^{-1})
F/W	space velocity (mol h^{-1} kg^{-1})
k_{ads}	rate constant of adsorption
k_{des}	rate constant of desorption
k	rate constant of surface reaction
K_{i}	adsorption coefficient
K'	equilibrium constant of surface reaction
n	number of kinetic runs
p^0	initial partial pressure
Q	sum of the squared deviations of the experimental from the calculated reaction rate $\sum_{i=1}^{n}(r_{\mathrm{exp}} - r_{\mathrm{calc}})^2$

r^0	initial reaction rate (mol h^{-1} kg^{-1})
R_A	relative reactivity of an alkylphenol (product of rate constant and adsorption coefficient) with respect to phenol
s	exponent in the denominator of rate equations, corresponding to the number of active centres taking part in rate-controlling step
W	weight of catalyst (kg)
x	degree of conversion
Y	slope of linear relation (*14*) between R_A and r^0_A/r^0_F
α, β	exponents at partial pressures of phenol and hydrogen in power low equation (*11*)
ϱ	correlation coefficient
σ^*	Taft polar substituent constant

Reaction components

A	alkylphenol or phenol generally
B	hydrogen
F	phenol
M	unstable intermediate of cyclohexadiene type in Scheme (*B*)
R	reaction product (cyclohexanone)

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