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Hydrogenolysis of Ethylbenzene over a Supported Nickel Catalyst Derived from Nickel Hydroaluminate

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The hydrogenolysis of ethylbenzene at 280–400°C has been compared to the hydrogenolysis of toluene previously studied on the same catalyst. The rate of the first demethylation of ethylbenzene (into toluene) is significantly larger than that of the second demethylation (into benzene) and of the rupture of the aromatic nucleus (into methane). The apparent activation energies for these three reactions are 36.1, 52.8, and 56.1 kcal mol^{-1}, respectively. The rates of the second demethylation and of the ring opening for ethylbenzene are of the same order of magnitude as those previously observed with toluene. These results are interpreted by the presence of two types of sites, one operative in dealkylation (nickel atoms) and the other active for ring opening (nickel atom ensembles). For the overall reaction of ethylbenzene–H_2 a reaction scheme of the "rake" type is proposed.

INTRODUCTION

The catalytic reforming process of oil produces large quantities of alkylaromatics. The dealkylation of these compounds is an important industrial reaction for the production of benzene (*1–3*). The hydrodealkylation of toluene as a model molecule has been the subject of many studies (*1, 2, 4, 5*), whereas research concerning the dealkylation of other alkylbenzenes was mostly done in the 1960s (*6–8*), in particular in Prague (*7, 8*) on Ni/Al_2O_3 catalysts. The main conclusion of this work was that the alkyl groups are demethylated stepwise by formation of an alkylbenzene with a shorter chain which undergoes further splitting in a similar manner. The kinetic data gave the best fit for the Langmuir–Hinshelwood-type model in which the rate-controlling step is a surface reaction of molecularly adsorbed alkylbenzene with hydrogen. The authors could not specify the form of this reactive hydrogen, whether adsorbed molecular or atomic or molecular by impact from the gas phase. In order to observe the very first step of the degradation, the conversion was maintained below 10% and in the kinetic data initial rates (by extrapolation) were involved. In the case of ethylbenzene it was considered that at 350°C there was a minimum contribution of the cleavage of the terminal bond to total conversion of 69% (giving toluene), whereas the 31% contribution (giving benzene) may suggest a *parallel* cleavage of the nonterminal bond. The sequential reaction of demethylation of toluene was not included in this second fraction. More recently Duprez *et al.* (*9*) also concluded in favor of a predominant chain-end rupture in hydrodealkylation of alkylbenzenes in the presence of supported Rh catalysts, and therefore of the adsorption of the hydrocarbon via terminal chain carbon. The rupture of the aromatic nucleus, which is a minor reaction, would proceed via a π-adsorption of alkylaromatic followed by its

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dehydrogenation and σ-adsorption through adjacent carbons of the ring on two neighboring metal atoms.

In the previous contribution from this Laboratory (*4*) a kinetic study of the hydrodemethylation of toluene in the presence of a Ni/Al_2O_3 catalyst, derived from a nickel hydroaluminate, was presented. A triangular reaction scheme was proposed for the system toluene–H_2 consisting of parallel (toluene → methane and toluene → benzene) reactions and a sequential (toluene → benzene → methane) reaction. It is of interest to compare the same catalyst in the system ethylbenzene–H_2 in order to establish to what extent the parallel and sequential reactions are produced by the catalyst.

EXPERIMENTAL

The details of the experimental procedure and the nature of the catalyst and reactants used were given previously (*4, 10*). We recall that the catalyst is obtained by thermal decomposition and then reduction of a nickel hydroaluminate Al_2O_3, 2NiO, nH_2O (with $n = 8.2$). The total Ni content by weight is 53.5% (Ni/(Ni + Al_2O_3)). The catalyst is 63% reduced at 500°C in H_2. This represents 32% of metallic nickel, an amount close to that (41%, degree of reduction not precised) in the catalysts of the Prague school (*8*). The BET surface area of the reduced catalyst is 218 $m^2\ g^{-1}$. The diameter of Ni particles, determined by magnetic measurements, is of the order of 7 nm (*10*).

The kinetic measurements were performed in the dynamic regime under atmospheric pressure and the reaction partners were analyzed by gas chromatography. A differential dynamic microreactor was used for small conversions (a few percent), whereas for higher conversions (above 10%) the gradientless dynamic reactor with recirculation was employed (*4, 11*) in order to avoid mass and heat transfer phenomena. It is recalled that in this reactor the conversion up to about 90% may be achieved without any concentration gradient. The increase of the conversion with the contact time, for a given partial pressure of the reactant, is linear for low conversions and less than proportional for higher conversions because of a more drastic decrease of the partial pressure of the reactant which is transformed into the reaction products. Another possible cause of a nonlinear conversion when the contact time increases is an inhibiting effect of the reaction products. It was indeed observed that benzene is an inhibitor of the hydrodealkylation of toluene (*12, 13*).

The rates of formation of various products in the system ethylbenzene (EtB)–H_2 are directly calculated from their partial pressures. These products are methane, toluene (T), and benzene (B), with a very small amount of ethane (representing less than 0.5% of CH_4 produced). The following overall reactions of ethylbenzene may be therefore assumed:

dealkylation (DA):

$$\mathrm{EtB} + \mathrm{H_2} \rightarrow \mathrm{T} + \mathrm{CH_4} \qquad \text{(I)}$$

$$\mathrm{EtB} + 2\mathrm{H_2} \rightarrow \mathrm{B} + 2\mathrm{CH_4} \qquad \text{(II)}$$

aromatic ring opening (AO):

$$\mathrm{EtB} + 11\mathrm{H_2} \rightarrow 8\mathrm{CH_4} \qquad \text{(III)}$$

The selectivities into toluene (S_T), benzene (S_B), and for the ring opening (S_{AO}) are calculated from

$$S_T = n_T/\Delta n_{EtB} \qquad (1)$$

$$S_B = n_B/\Delta n_{EtB} \qquad (2)$$

$$S_{AO} = \tfrac{1}{8}(n_{CH_4} - (n_T + 2n_B)/\Delta n_{EtB} \qquad (3)$$

where n_T, n_B, and n_{CH_4} are the numbers of moles of toluene (T), benzene (B), and methane contained in an analyzed volume and determined by gas chromatography, and Δn_{EtB} is the number of moles of ethylbenzene (EtB) consumed in the reactor. For the gradientless reactor (high conversion) this quantity is directly available by gas chromatography, whereas for the

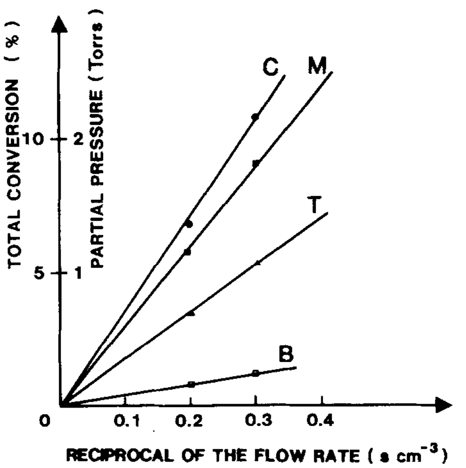


FIG. 1. Total conversion and partial pressures of reaction products in a differential reactor at 353°C for a partial pressure of ethylbenzene of 12.4 Torr, as a function of the contact time (or the reciprocal of the flow rate). C, total conversion; M, pressure of methane; T, pressure of toluene; B, pressure of benzene.

differential microreactor (low conversion) it is calculated from the product balance:

$$\Delta n_{EtB} = \tfrac{1}{8}(n_{CH_4} + 7n_T + 6n_B) \qquad (4)$$

RESULTS

1. Hydrogenolysis of Ethylbenzene

(*a*) *Influence of the temperature.* Preliminary experiments in the differential microreactor showed that above 280°C the hydrogenation of the aromatic nucleus becomes negligible. The only reactions observed in the range 280–400°C are (I), (II), and (III). Although hydrogenation of aromatic hydrocarbons is not thermodynamically favored above 280°C this reaction is fast and the saturated ring could be an intermediate in the ring opening (*12, 14, 15*). However, a reverse scheme is preferred by Duprez *et al.* (*9*) who consider a dehydrogenated diadsorbed aromatic ring as a precursor for the ring opening. Figure 1 shows that at 353°C for conversions not exceeding 12% the partial pressures of products (benzene, methane, and toluene) are proportional to the contact time or to the reciprocal of the flow rate. For any product, the rate of formation is therefore constant within the contact time range employed. The chemical regime is thus well observed. The results plotted in Fig. 2 may be compared with those obtained for higher conversions in a gradientless reactor used as an integral reactor (see below). On the ordinate are plotted the conversions into the reaction products (T, B, and AO) and the total conversion is plotted on the abscissa. In this representation, the slope of these curves for zero total conversion gives the rate of formation of products in the initial conditions (in the absence of the reaction products). Table 1 gives the temperature dependence of the rates of formation of toluene (R_T), of benzene (R_B), of the aromatic ring rupture (R_{AO}), and of the overall conversion (R_{TOT}). The initial partial pressure of the reactant (EtB) in the differential microreactor was in all cases 12.4 Torr (1 Torr = 133.3 Pa) and the mass of the catalyst varied in the limits 4–12 mg, giving a conversion not exceeding 7%.

The rates of Table 1 give linear Arrhenius plots and the corresponding apparent activation energies are listed in the last line of the table. The calculated selectivities are shown in Fig. 3. Toluene is always the main

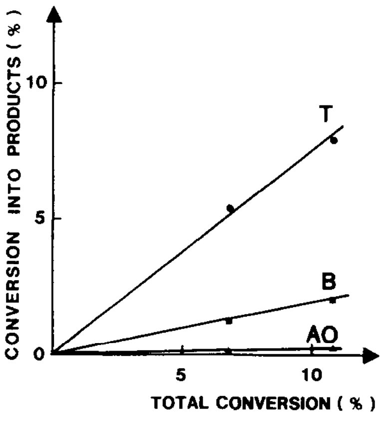


FIG. 2. The conversion into the reaction products in a differential reactor, for a partial pressure of ethylbenzene of 12.4 Torr at 353°C, as a function of the total conversion. T, toluene; B, benzene; AO, aromatic ring opening.

TABLE 1

Influence of Temperature on Rates of Formation of Reaction Products (P_{EtB} = 12.4 Torr)

Temp. (°C)	R_T	R_B	R_{AO}	R_{TOT}
	(10^{-6} mol g^{-1} s^{-1})			
288	0.502	0.033	0.003	0.538
303	1.303	0.113	0.008	1.424
321	3.789	0.473	0.040	4.302
335	7.367	1.147	0.130	8.644
352	17.170	3.985	0.445	21.600
Activation energy (kcal/mol)	38.2	52.8	56.1	41.0

reaction product but the selectivity into toluene [Eq. (1)] decreases when the temperature increases (curve T), whereas the selectivity into benzene [Eq. (2)] increases (curve B) (from 6 to 26%). Simultaneously, the aromatic ring opening reaction [Eq. (3)] becomes slightly more important (curve AO). The amount of ethane formed, probably by the reaction

$$EtB + H_2 \rightarrow B + C_2H_6$$

and possibly in the reaction of ring opening (together with very small amounts of C_3, C_4, . . .), never exceeded 0.5% of the amount of CH_4 detected.

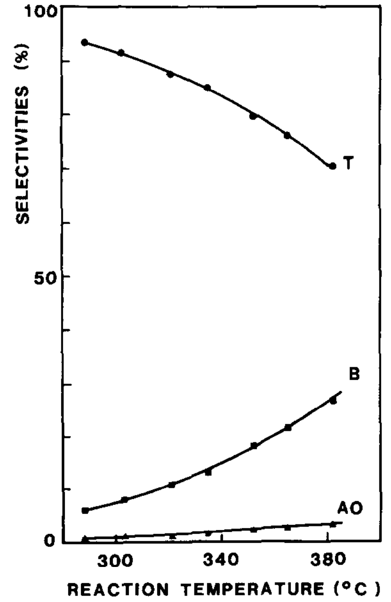


FIG. 3. The modification of the selectivities with the temperature of the reaction in a differential reactor. T, toluene; B, benzene; AO, aromatic ring opening.

(*b*) *Influence of the contact time.* The results of Fig. 3 show that for small conversions (less than 7%) S_B and S_{AO} increase with the temperature but toluene is always a major reaction product. In the first approach it is attractive to consider that the reaction proceeds by a stepwise degradation of the alkyl chain, EtB giving T, which in turn is hydrodemethylated into B. The rate of the first hydrodemethylation, which is initially predominant, increases less with the temperature than the rate of the second demethylation. Indeed, the low reactivity in the hydrodealkylation of toluene compared with that of ethyl- or *n*-propylbenzene has been observed previously (*8*).

When the contact time is increased (increased conversion) at a given temperature, the selectivity into benzene should increase and that into toluene decrease because of the time allowed for the sequential hydrodemethylation. Also, it is of interest to follow these selectivities for higher conversions in the gradientless reactor. Table 2 gives the results observed at 343°C with an initial partial pressure of EtB of 25 Torr and a mass of the catalyst of 70.6 mg, the

TABLE 2

Selectivities into Reaction Products for Higher Conversions at 343°C (P_{EtB} = 25 Torr)

Contact time (10^{-2} s)	Conversion (%)	S_T (%)	S_B (%)	S_{AO} (%)	R_{TOT} (10^{-6} mol g^{-1} s^{-1})
3.13	16.2	55.0	32.9	12.1	7.4
5.26	21.4	52.6	34.1	13.3	5.8
9.22	30.0	52.1	34.3	13.6	4.7
13.27	37.0	49.8	35.0	15.2	4.0

conversion depending nonlinearly on the contact time (*11*).

The overall rate (R_{TOT}) decreases when the contact time (and the conversion) increases because of (i) the decrease in the reactor of the partial pressure of the reactant which is consumed, and (ii) an inhibiting effect of aromatic products (toluene and benzene) (*12, 13*). An extrapolation for zero conversion gives $R_{TOT} = 11 \times 10^{-6}$ mol g^{-1} s^{-1} which is a rate close to that observed at a comparable temperature in the differential microreactor (Table 1) for the partial pressure 12.4 Torr (between 8.644 and 21.600 mol g^{-1} s^{-1}).

When the conversion increases from 16 to 37% (Table 2) S_T decreases, whereas S_B and S_{AO} increase. Such a behavior, as well as the results of Fig. 3, tend to show that the dealkylation of ethylbenzene into toluene precedes the dealkylation of toluene into benzene which in turn precedes the aromatic ring opening. The successive character of these reactions is better perceived for conversions close to 100%. For this purpose, the gradientless reactor was used without the recirculation of reaction partners. This procedure converts this reactor into an integral reactor. With the partial pressure of ethylbenzene of 17 Torr, conversions up to 90% may be registered. The results at 350°C are represented in Fig. 4, in the same way as for Fig. 2. The conversion into toluene (the ordinate) goes through a maximum (curve T) for a total conversion of about 80% (the abscissa). Above, benzene becomes the major product (curve B). Simultaneously, the production of methane from the aromatic ring opening (curve AO) becomes accentuated. These results, and in particular the maximum in the formation of toluene, confirm the successive character of the previous reactions.

2. *Hydrogenolysis of Ethane*

If ethane is formed directly by hydrogenolysis of ethylbenzene into benzene it would not be stable (almost no ethane is found) but converted into methane. This behavior would mean that a parallel step (EtB → B + C_2H_6) in the hydrodealkylation is added and that the cleavage of the terminal bond (to toluene) represents only, at low conversion, at, say, 352°C (Table 1), 80% of the total conversion, whereas about 20% proceeds through the cleavage of the nonterminal bond. Also hydrogenolysis of ethane was tested in both reactors.

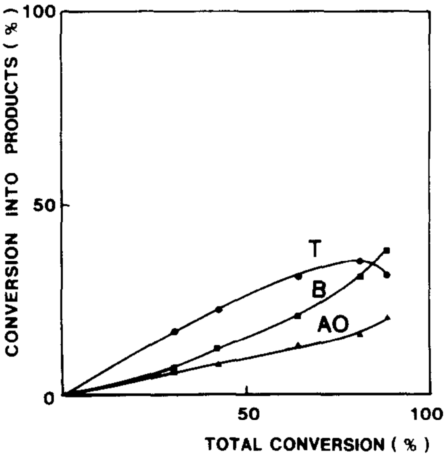


FIG. 4. The conversion into the reaction products in an integral reactor at 350°C, for a partial pressure of ethylbenzene of 17 Torr, as a function of the total conversion. T, toluene; B, benzene; AO, aromatic ring opening.

(*a*) *Differential microreactor.* At 350°C the partial pressure of ethane in a flow of H_2 is fixed at 0.65 Torr. This pressure is that which would result from the direct dealkylation of ethylbenzene into benzene, in the conditions which lead to the results in Fig. 1.

The observed rate of hydrogenolysis of ethane for a conversion of 2% (mass of catalyst = 15.8 mg, contact time = 0.33×10^{-2} s) is 0.3×10^{-6} mol g^{-1} s^{-1}. If, in the same conditions, a pressure of 17 Torr of ethylbenzene in addition to the pressure of ethane (0.65 Torr) is established in the flow of reactants, the registered pressure of methane (1.2 Torr) can result exclusively from the interaction between ethylbenzene and hydrogen because the pressure of ethane (0.65 Torr) is the same in the inflow and outflow. For pure ethane, the partial pressure of methane for 2% conversion was only of the order of 0.025 Torr.

(*b*) *Gradientless reactor.* A test performed in this reactor (with recirculation) at 350°C, with a mass of catalyst of 49.2 mg, a partial pressure of ethane of 2.1 Torr and a contact time of 2×10^{-2} s, gives the value of the rate of hydrogenolysis 0.8×10^{-6} mol g^{-1} s^{-1} for a conversion of 30%. This rate is of the same order of magnitude as in the differential reactor. If its value is higher (0.8×10^{-6} mol g^{-1} s^{-1} vs 0.3×10^{-6} mol g^{-1} s^{-1}) it is because of a higher partial pressure of ethane (2.1 vs 0.65 Torr). However, it is, at least, one order of magnitude smaller than the rate of the hydrodealkylation of EtB at 352°C (Table 1) assuming that it gives directly benzene (R_B). Therefore, the results of the hydrogenolysis of ethane at any conversion show that this reaction is slow and a direct hydrogenolysis of EtB into benzene cannot represent 20% of the total conversion (see above). This conclusion assumes that in the direct conversion of EtB into ethane the adsorption–desorption equilibrium of the generated ethane is established. This hypothesis seems reasonable considering that the adsorption–desorption equilibrium of the reactants seems to correspond to the kinetic data where the slowest step is the interaction of the adsorbed EtB with hydrogen (*7*) and more arguments in favor of this are developed below.

DISCUSSION

The present results should be discussed taking into account previous results on the same catalyst concerning the hydrogenolysis of toluene and of benzene (*4*).

1. Activity and Selectivity

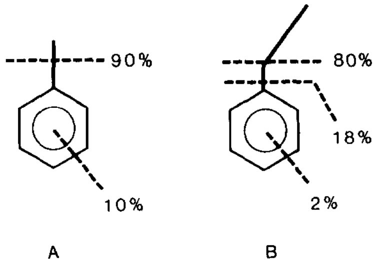
The dealkylation of ethylbenzene into toluene (and methane) is the main reaction observed at 350°C for total conversion not exceeding 80% (Fig. 4). Its rate observed at 352°C in the initial conditions (low conversion, differential reactor) is 17.17 mol g^{-1} s^{-1} (Table 1). If toluene is the reactant, its dealkylation into benzene (and methane) in the same conditions is about 8 times slower (rate: 2.22×10^{-6} mol g^{-1} s^{-1}) (*4*). This lower reactivity of toluene was already observed previously (*8*). Assuming that in the hydrogenolysis of ethylbenzene the first reaction product is toluene (and methane) which then may be demethylated into benzene, the rate of formation of benzene from ethylbenzene would be very close to the rate of formation of benzene from toluene. Table 1 shows indeed that the rate of formation of benzene (R_B) at 352°C from EtB is 3.985×10^{-6} mol g^{-1} s^{-1} which is very close to the rate of formation of benzene from toluene at 350°C (2.22×10^{-6} mol g^{-1} s^{-1}) (*4*). The slight difference between these two rates is not significant considering a slight difference in the reaction temperatures. The nonequilibrated adsorption–desorption of toluene produced from ethylbenzene cannot be envisaged as toluene is the most abundant product in the gas phase and its rate of demethylation into benzene is smaller than that of EtB into toluene. Moreover, EtB is more strongly adsorbed on Ni than toluene (*17, 18*). Similarly, the rate of the aromatic ring opening (R_{AO}) for ethylbenzene at 352°C is 0.445×10^{-6} mol g^{-1} s^{-1} (Table 1) which is of the same order as that for toluene at 350°C (0.26×10^{-6} mol g^{-1} s^{-1}) (*4*). This tends to show that the precursor in the degradation reaction of the aromatic nucleus is the same (benzene) for both reactants, EtB and toluene.

The difference observed in the reactivities of ethylbenzene and of toluene is therefore related to the rupture of the first methyl group, which is much faster for ethylbenzene. This result is in agreement with the C—C bond energies which for the terminal methyl group are 63 kcal mol^{-1} in the case of ethylbenzene and 87 kcal mol^{-1} for toluene (*16*). Simultaneously, it is observed that ethylbenzene is more strongly adsorbed than toluene on the surface of nickel (*17, 18*).

Another argument in favor of the first demethylation of ethylbenzene into toluene may be found in the activation energies. In the case of toluene as reactant, the activation energies of formation of benzene and of the aromatic ring rupture are practically the same (36 kcal mol^{-1}) (*4*). Now, this value is very similar to that observed for the first demethylation of ethylbenzene as reactant into toluene (38.2 kcal mol^{-1}, Table 1). However, the second demethylation of ethylbenzene into benzene and the aromatic ring opening present much higher activation energies (52.8 and 56.1 kcal mol^{-1}, Table 1). This may be surprising if it is considered that the formation of benzene from EtB proceeds sequentially, through the initial formation of toluene. However, it should be recalled that EtB being more strongly adsorbed than toluene, the activation energy of the reaction of toluene in the presence of EtB reflects the heat of adsorption of this last reactant. The rate controlling step is very likely a surface reaction of adsorbed aromatic molecules and H_2 (*6, 7*).

The selectivities in the rupture by hydrogenolysis of various C—C bonds at 350°C for toluene, as revealed at low conversions, are illustrated by Scheme 1A (*4*), whereas for ethylbenzene in the present work (Fig. 3), they are illustrated by Scheme 1B.

For toluene these selectivities are almost constant with the temperature (*4*) in the range 300–350°C, whereas for ethylbenzene S_{T} decreases and S_{B} and S_{AO} increase (Fig. 3). This behavior reflects the differences in the activation energies in the demethylation and ring opening of both reactants, discussed previously. For ethylbenzene S_{AO} at 350°C is markedly smaller (2%) than for toluene (10%). However, the ratio of the selectivity into the demethylation (the first) of toluene and (the second) of EtB and the selectivity of the ring opening, $S_{\mathrm{B}}/S_{\mathrm{AO}}$, is 9 for both reactants (90/10 and 18/2). This brings another argument in favor of the sequential demethylation and hydrogenolysis of ethylbenzene. For this last reactant, a fast hydrodemethylation into toluene precedes the reactions of the second demethylation into benzene and, finally, of the ring opening.



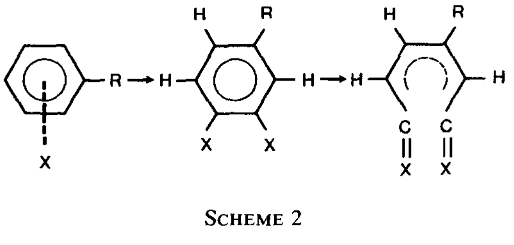
SCHEME 1

2. Mechanisms and Reaction Schemes

The great selectivity observed in the sequential hydrodealkylation of alkylbenzene over nickel [this work and Refs. (*1, 4, 7, 8, 19*)] and over Group VIII metals (*1, 5, 9, 12*) suggests that these hydrocarbons are preferentially adsorbed perpendicularly to the metal surface by fixation of the terminal carbon of the alkyl chain (*5, 9*). The presence of hydrogen may favor the formation of such species by competitive adsorption of H_2 and of alkylbenzenes on metallic sites (*6, 9*). The hydrocarbon molecules are forced to occupy a minimum metallic surface (*9*) and the σ-adsorption is favored by comparison with the π-adsorption. Such a behavior also underlines that multiple hydrogenolysis is not liable to occur easily. The present work shows that the formation of toluene as a major product and the absence of ethane (which cannot be easily hydrogenolyzed into methane, see above) result from the sequential demethylation of ethylbenzene. This is in agreement with the previous considerations concerning the preferential adsorption on nickel of alkylbenzenes through the aliphatic carbon. However, the aromatic ring opening implies species adsorbed with multiple bonds between the carbons of the ring and the metal. It has been suggested (*9*) that the precursors of these species are π-complexes, formed by interaction between the nucleus and the metal. The slow step of the ring opening is supposed to occur by the transformation of the π-complexes into σ-adsorbed species according to Scheme 2.

Such a transformation requires sites formed by a relatively high number of adjacent metallic atoms (>2), whereas the dealkylation would occur on sites formed by one or two atoms (*9*). This hypothesis explains also a higher selectivity in the steam dealkylation of toluene in the presence of small particles of Rh, rather than coarse particles (*20*), where the density of sites formed by one or two atoms only is higher. On the other hand, the same hypothesis is in agreement with the experimentally observed evidence concerning the same activity in the ring opening of various alkylbenzenes during their conversion in H_2 or in H_2O vapor over Rh catalysts of the same dispersion (*9*). The overall rate (R_{TOT}) depends on the nature of the alkyl group but the rate of the ring opening on multiple sites is the same for any alkyl group.

For the nickel catalyst used in this work the rate of demethylation of ethylbenzene into toluene at 350°C is 8 times higher than the rate of demethylation of toluene into benzene [Table 1 and Ref. (*4*), see above], whereas the rates of the aromatic ring opening for ethylbenzene and for toluene are of the same order (see above). These results tend to show that on nickel, the aromatic nucleus opening also occurs on specific sites, as for Rh (*9, 20*), which are different from the sites operating in dealkylation. For benzene the rate of the ring opening is much higher than for ethylbenzene or for toluene. This situation may result, in the case of alkylaromatics, from the competition in the π-adsorption of the nucleus and the terminal alkyl carbon σ-adsorption of the alkylaromatics (*21*).



SCHEME 2

It therefore seems that as long as the alkylaromatic is not hydrodealkylated (eventually in steps) the nucleus cannot be open. Under comparable experimental conditions (350°C, atmospheric pressure) predominant stepwise degradation on nickel catalysts has also been reported for the hydrodealkylation of alkylbenzenes (*7, 8, 19*) and alkylnaphthalenes (*22*). However, unlike in the present work, no fission of the aromatic nucleus was reported in these papers. This omission may arise from (i) a difference in the morphology of catalysts which imposes the distribution of the two types of sites, working respectively in the hydrodealkylation and in the ring opening (see above), and (ii) a small extent of ring opening could escape the investigation. Taking into account the assumptions published by the Bazant school (*7, 8, 19*) the reaction scheme for the hydrodealkylation of EtB would be of a triangular type, **I**.

$$\begin{tikzcd} & \mathrm{T} \arrow[dd] \\ \mathrm{EtB} \arrow[ur, "S_T"] \arrow[dr, "S_B"'] & \\ & \mathrm{B} \end{tikzcd}$$

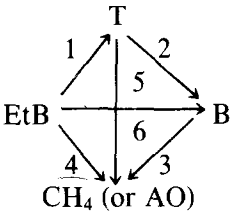
I

At 10% conversion the authors reported the selectivity value $S_T = 69\%$ as a minimum contribution for the terminal carbon cleavage. $S_B = 31\%$ was considered as evidence of the parallel cleavage of a nonterminal carbon. The results obtained in the present work suggest that all reactions of EtB are of a sequential type and that the triangular scheme should be replaced by **II**.

$$\begin{array}{ccccccc} \mathrm{EtB} & \rightarrow & \mathrm{T} & \rightarrow & \mathrm{B} & \rightarrow & \mathrm{CH_4(or\ AO)} \\ \upharpoonleft\downharpoonright & & \upharpoonleft\downharpoonright & & \upharpoonleft\downharpoonright & & \upharpoonleft\downharpoonright \\ \mathrm{EtB(g)} & & \mathrm{T(g)} & & \mathrm{B(g)} & & \mathrm{CH_4(g)} \end{array}$$

II

This "rake" scheme (*23*) accounts for the presence in the gas phase of EtB, T, B, and CH_4 and practically the absence of ethane. The simultaneous parallel reactions 4, 5, 6 in scheme **III** have very small probability of occurring, at least under our experimental conditions.



III

CONCLUSIONS

In the presence of an alumina-supported nickel catalyst, prepared from nickel hydroaluminate, the interaction between ethylbenzene and hydrogen, at 280–400°C, leads mainly, for conversions smaller than 80%, to toluene. Benzene is a minor product and methane is obtained from successive demethylations of ethylbenzene. Only very small fraction of this product comes from the aromatic nucleus opening. The rate of the overall conversion of ethylbenzene is higher than that observed for toluene, reported previously (*4*). This behavior results from the high rate of the first demethylation of ethylbenzene into toluene. The second demethylation (into benzene) and the aromatic ring opening proceed with rates comparable to those observed with toluene (*4*). This difference in the reactivity of ethylbenzene and of toluene may be explained by a smaller energy of the C—C bond for the methyl group in ethylbenzene than in toluene. Also, the adsorption strength on the nickel surface is higher for ethylbenzene than for toluene. The registered selectivities into toluene, benzene, and aromatic ring opening suggest that in the presence of hydrogen, ethylbenzene is adsorbed mainly by the terminal carbon of the alkyl group. Any fraction of the resulting benzene which would be adsorbed through the carbon atoms of the aromatic ring and would require multiple nickel atoms sites is then hydrogenolyzed into methane (aromatic ring opening). A reaction scheme of the "rake" type is proposed to interpret the observed selectivities in the hydrogenolysis of ethylbenzene.

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