

Alkylations of Arenes with Ethylene over H-ZSM-5 and Mordenite-H Catalysts

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Attempts were made to alkylate acetophenone, benzene, benzonitrile, bromobenzene, chlorobenzene, ethylbenzene, fluorobenzene, iodobenzene, methoxybenzene, nitrobenzene, toluene and α,α,α -trifluorotoluene with ethylene over H-ZSM-5 and mordenite-H catalysts at 400 and 250 °C, respectively.

Over H-ZSM-5 benzene, bromobenzene, chlorobenzene, ethylbenzene and toluene gave monoethylarenes as the major product (95-100 %) with the *para* product as the dominant isomer (87-95 %). Over mordenite-H benzene, bromobenzene, chlorobenzene and toluene reacted. The monoethylarenes were again the major product (85-95 %) but the isomer distributions were close to the thermodynamically controlled ones due to isomerisation of the initially formed products. Over H-ZSM-5 the results indicated the reaction to be of a Friedel-Crafts type. It was proposed that the product composition was determined by the chemical reaction, not by the rate of diffusion of the products.

The alkylation of aromatic hydrocarbons over acidic heterogeneous catalysts is of great practical importance.^{1,2,3} The ethylation of benzene is particularly so, but the formation of xylenes from benzene or toluene is also a significant industrial process.^{4,5} The heterogeneous catalysts used are of the zeolite type with the new ZSM-5 catalyst showing high selectivity and also a long life time.

It has generally been assumed that the mechanism of heterogeneously catalysed alkylations is similar to that of analogous reactions run in solution.^{2,6} This means that the alkylating agent, *e.g.* ethylene, reacts with the catalyst to form a highly polarised complex which then reacts with the arene in an electrophilic aromatic substitution. To test this we have reacted benzene and several monosubstituted benzenes with ethylene over two different zeolite catalysts. If the above hypothesis is correct, with the formation of the Wheland intermediate as the rate determining step, we would expect the reactivity of the arenes to be correlated by the Hammett equation. We would also expect the substitution pattern to be similar to that observed for Friedel-Crafts reactions in solution, that is, predominance of the *ortho* and *para* isomers over the *meta*. The results would also indicate the scope and limitations of heterogeneously catalysed alkylations of arenes.

RESULTS

The two catalysts used in this investigation were the proton forms of ZSM-5 (H-ZSM-5) and of mordenite (Zeolon 200 H). The reactions were run in a continuous tubular reactor with a arene/ethylene ratio of 7 to avoid polymerisation of ethylene.⁶ The partial pressures of the reactants and the amounts of catalysts were adjusted to give <10 % conversion of ethylene. By this method, the partial pressures of the reactants were essentially constant throughout the catalyst bed (differential conditions). The reactor was run at atmospheric pressure, the partial pressures of the reactants being controlled by using nitrogen as a carrier gas.

H-ZSM-5. Over this catalyst iodobenzene, fluorobenzene, benzonitrile, acetophenone, nitrobenzene, α,α,α -trifluorotoluene and methoxybenzene did not react under the conditions applied. On the other hand, benzene, toluene, ethylbenzene, chlorobenzene and bromobenzene were all alkylated, the *p*-ethyl isomers being the major products for the four last compounds. The reactions were performed at 400 °C. No reaction took place at 250 °C. (Table 1). The selectivities for monoalkylation were from 95 to 100 %. The yields of product were linearly related to the mass of catalyst (Fig. 1). The catalyst slowly lost activity (after 100 min reaction time, 95 % of maximum).

Mordenite-H. The same compounds were investigated using mordenite-H as a catalyst. Only benzene, toluene, chlorobenzene and bromobenzene were alkylated. The selectivities for monoalkylation were almost as high as with H-ZSM-5 as catalyst (85-95 %) but the isomer distributions were different with high yields of the *meta* isomers, especially at higher conversions (Table 3). This was partly caused by isomerisation, as shown by the isomerisation reactions of ethylenes over H-mordenite (Table 4). The alkylation reactions were performed at 250 °C, at which temperature no reaction took place over H-ZSM-5. However, the activity was lost more rapidly than that of H-ZSM-5 (after 100 min reaction time, 65 % of maximum activity).

DISCUSSION

The results using the two catalysts were rather different. We will discuss them separately before attempting to reach a final conclusion.

H-ZSM-5. This catalyst, developed for the formation of hydrocarbons from methanol is also a remarkable catalyst for the alkylation of aromatic compounds. With chemically treated, or especially large-crystal H-ZSM-5, a high yield of *p*-xylene was obtained from toluene and methanol.⁴ With untreated, or small crystal catalysts, isomer mixtures with compositions close to the thermodynamically controlled ones were obtained.^{3,4,5} The pore system in ZSM-5 consists of two types of intersecting channels, one type being straight with elliptical (5.1-5.6 Å) openings, the other being sinusoidal with near-circular (5.4-5.6 Å) openings. The channel intersections have a free space of larger dimensions (*ca.* 9 Å).⁷

In our experiments, the reactivity of the arenes were parallel to that found in liquid phase Friedel-Crafts alkylations, and arenes more deactivated than the halobenzenes did not react. The reason for the inertness of methoxybenzene may have been strong hydrogen bonds from the acidic catalyst to the methoxy oxygen leading to deactivation of the ring.

For the arenes that were alkylated, monoalkylation was the dominant reaction with a selectivity from 95 to 100 %. Furthermore, the ethylenes formed contained 85 to 95 % of the *para* isomer (Table 1). Scanning electron microscopy showed the H-ZSM-5 crystals to

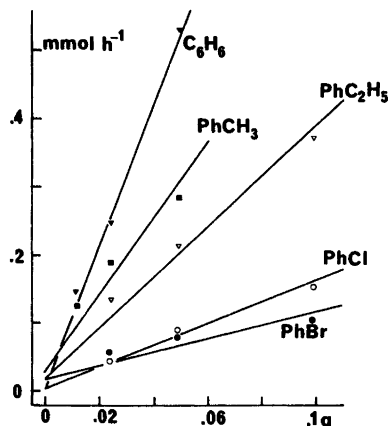


Fig. 1. Yield of *p*-ethylarenes (mmol h^{-1} , ethylbenzene from benzene). Curves are best fits from linear regressions (Table 1).

be from 1 to 2 μm , that is, of a size that would be expected to give a high yield of the *para* isomers.⁴ However, if we increased the conversion of toluene from *ca.* 0.3 mmol h^{-1} (Fig. 1) to 1.5 mmol h^{-1} by increasing the amount of catalyst, the *para/meta* ratio decreased from 87/11 to 75/25. This indicates that the initially formed product is the *para* isomer which subsequently isomerises. We propose this isomerisation to take place on the surface of the catalyst crystals where there are no steric restrictions on the transition state (as opposed to in the micropores). This may also explain the lower regioselectivity of small catalyst crystals as compared to larger ones. Smaller crystals have shorter micropores than larger ones,⁴ but also larger outer surface area per weight unit catalyst.

The high *para* selectivity has been explained as an effect of the 10^4 higher rate of diffusion of the *para* isomer as compared to the *ortho* and *meta* ones. The reaction was believed to take place in the intersections of the channels whereby the products rapidly isomerised to the thermodynamically stable *ortho-meta-para* mixture. The rate of diffusion out of the intersections would then determine the observed product composition.⁸ As further evidence for this, it was pointed out² that benzene was alkylated faster than toluene and this was contrasted to the fact that in the liquid phase toluene is intrinsically more reactive toward alkylation.

Table 1. Alkylation of benzene and monosubstituted benzenes with ethylene over H-ZSM-5. Temperature: 400 °C; $p_{\text{arene}}=90$ Torr; $p_{\text{ethylene}}=13$ Torr; feed rate arene: 53 mmol h^{-1} . Atmospheric pressure, inert gas: N_2 .

Arene	Yield of <i>para</i> ethylarene $\text{mmol h}^{-1}\text{g}^{-1}$ ^a	Isomer distribution of ethylarenes %.		
		<i>ortho</i>	<i>meta</i>	<i>para</i>
Benzene	10.47 (0.999)	—	—	—
Toluene	5.43 (0.968)	2	11	87
Ethylbenzene	3.60 (0.990)	3	7	90
Chlorobenzene	1.54 (0.995)	0	5	95
Bromobenzene	0.99 (0.923)	1	4	93

^a Linear regressions from data in Fig. 1. Correlation coefficient *r* in parentheses.

Table 2. Linear free energy correlation of the reactivities of arenes in ethylation over H-ZSM-5 at 400 °C. $C_6H_5-X+CH_2=CH_2 \rightarrow C_2H_5-C_6H_4-X^a$

X	$\log f_p$	σ	σ^+
H	0	0	0
CH ₃	0.493	-0.17	-0.31
C ₂ H ₅	0.314	-0.15	-0.30
Cl	0.055	0.23	0.11
Br	-0.247	0.23	0.15

^aUse of σ : Slope -1.40, intercept 0.140, $r = -0.920$. Use of σ^+ : Slope -1.30, intercept 0.01. $r = 0.966$.

If this was the correct explanation, and if the rate of diffusion was determined by the size of the molecule, one would expect, *e.g.*, toluene and bromobenzene to react at comparable rates as their critical dimensions are similar. This was not the case in our experiments (Table 1). If, on the other hand, the chemical reaction was rate determining the results in Table 1 would be in qualitative accordance with results from solution alkylations of arenes, with alkylbenzenes more reactive than halobenzenes. For Friedel-Crafts alkylations in solution, the complex between acidic catalyst and alkylating agent is believed to be formed in a rapid pre-equilibrium followed by the slow formation of the Wheland intermediate.⁹ If this was the case in the reaction over H-ZSM-5, the rates of ethylation would be expected to follow a linear free energy relationship.

All the alkylations were run under the same differential conditions. If the mechanism was the same for all five reactions, the conversion to product would be proportional to the rate of reaction. We will therefore assume the calculated yield per hour and gram of catalyst (Table 1) to be proportional to the rate of reaction of each arene reacted.

The partial rate factors, f_p , for the *para* substitutions will be $f_p = 6(r_X/r_H)$ where r_X is the rate of reaction of the X-substituted benzene and r_H that of benzene. The ratio is multiplied by a statistical factor of six. If the formation of the Wheland intermediate was rate determining, one would expect $\log f_p = \rho\sigma^+$ to hold. In Table 2 the parameters from a linear regression of this and also for $\log f_p = \rho\sigma$ are given. The use of σ^+ gave the best fit, indicating the transition state to have a well developed positive charge. The ρ for the reaction is not large (-1.30) but the reactions were run at 400 °C. Assuming a temperature independent activation energy, this would correspond to $\rho = -2.90$ at 25 °C. Friedel-Crafts alkylations in solution have low intermolecular and intramolecular selectivities. Only a few arenes have been alkylated by olefins, but from the limited data⁹ the ρ value found in the reaction over H-ZSM-5 appear to be normal for this type of reactions.

The Hammett σ^+ plot therefore indicates the reaction over H-ZSM-5 to go by a mechanism similar to that in solution: A positively charged complex is formed between the acidic sites in the catalyst and ethylene which reacts with the arene in a slow step to give the product. We therefore propose that the high yields of *para* isomers are due to a reaction where the formation of the Wheland intermediate for both *ortho* and *meta* isomers are sterically inhibited (restricted transition state selectivity);⁷ not the higher rate of diffusion from the intersections of the *para* isomers. Further, we see that the rates of reaction of toluene and benzene are in the expected order once the statistical factor is taken into account.²

Mordenite-H. This catalyst (Zeolon-H) is characterised by a system of parallel channels (7.1×5.9 Å).¹² Alkylations of benzene over H-mordenite has been reported. The major

Table 3. Alkylation of benzene and monosubstituted benzenes with ethylene over H-mordenite. Temperature: 250 °C. $P_{\text{arene}}/P_{\text{ethylene}}=7$. Atmospheric pressure. Inert gas: N₂. Yields in mmol h⁻¹g⁻¹.

	Reactions conditions				Toluene			Chlorobenzene			Bromobenzene					
	Amount of catalyst/g	P_{arene} Torr	Total feed rate/mol h ⁻¹ g ⁻¹	Benzene Yield	Yield	Isomers %			Yield	o	m	p	Yield	o	m	p
						o	m	p								
1.	3	100	0.144	1.78	1.31	21	71	8	1.40	58	22	20	0.55	32	40	28
2.	1	30	12.6	0.86	0.96	9	75	16	0.49	64	20	16	0.37	30	40	30
3.	0.5	12	7.46	0.97	1.10	12	62	26	0.52	58	18	24	0.42	31	38	31
4.	0.2	12	18.75	0.43	0.46	12	60	28	0.20	52	12	36	0.19	30	40	30

product below 300 °C was ethylbenzene, although *m*-diethylbenzene and naphthalene were both present at 150 °C (8 % each). The rate of reaction was correlated to the concentration of Brønsted centers, and the proton transfer from the catalyst to ethylene was proposed as the rate determining step.⁶

In our experiments, the reactivities were again parallel to those of Friedel–Crafts alkylations in solution, but only four arenes reacted over H-mordenite; benzene, toluene, chlorobenzene and bromobenzene. Even though reactivities of the arenes were parallel to those found in solution, the substitution patterns were far from those of typical electrophilic aromatic substitutions. At conversions only one tenth of those obtained over H-ZSM-5, the *meta* isomers were the dominant products. Isomerisations are well known over this type of catalyst and isomerisation experiments (Table 4) showed that at conditions corresponding to runs 1 and 2 in Table 3, the same isomeric mixtures were obtained from all three ethylarene isomers, presumably the thermodynamically most stable ones. In the two last series of the isomerisation experiments, the conditions were close to those of the last two runs in the alkylation series, that is with very low conversion. Under these conditions, the ethylarenes isomerised only from ten to twenty percent (Table 4). The alkylations under these conditions might therefore have given results close to those of the originally formed product mixture. Nevertheless, the results in Table 3 indicate that this may only be partly true. For toluene and bromobenzene the product ethylarenes were richer in the *meta* isomers than expected from a Friedel–Crafts alkylation, even at the lowest conversions (runs 3 and 4 in Table 3). For chlorobenzene a more normal distribution was obtained. The isomerisation experiments showed the ethyltoluenes and bromoethylbenzenes to isomerise at higher rates than the corresponding chloroethylbenzenes (Table 4). As the ethylation of chlorobenzenes gave results closest to those expected for a Friedel–Crafts reaction, one can not exclude that the reactions of the two other arenes (toluene and bromobenzene) may have resulted in similar initial mixtures followed by partial isomerisations. The apparent discrepancy between this and the isomerisation experiments could be explained by slow diffusion in the micropores. In that case, the ethylarenes in the isomerisation experiments would not have time to diffuse into the pores to react completely and the products from the

Table 4. Isomerisation of ethylarenes over H-mordenite at 250 °C. Inert gas: N₂.

Ethylarene	Isomer distribution after reaction %		
	<i>ortho</i>	<i>meta</i>	<i>para</i>
<i>o</i> -Ethyltoluene ^a	11	58	31
<i>m</i> -Ethyltoluene ^a	11	56	33
<i>p</i> -Ethyltoluene ^a	11	58	31
<i>o</i> -Chloroethylbenzene ^a	50	35	15
<i>p</i> -Chloroethylbenzene ^a	8	58	34
<i>o</i> -Bromoethylbenzene ^a	20	55	25
<i>p</i> -Bromoethylbenzene ^a	20	55	25
<i>p</i> -Ethyltoluene ^b	5	13	82
<i>p</i> -Bromoethylbenzene ^b	2	2	96
<i>o</i> -Bromoethylbenzene ^b	78	14	8
<i>p</i> -Chloroethylbenzene ^b	5	10	85

^a Reaction conditions: 2 g cat., $p_{\text{arene}}=0.68$ Torr, Total feed rate: $0.75 \text{ mol h}^{-1}\text{g}^{-1}$. ^b Reaction conditions: 0.2 g cat., $p_{\text{arene}}=13$ Torr, Total feed rate: $18.75 \text{ mol h}^{-1}\text{g}^{-1}$.

alkylation reactions would have time to partly isomerise before leaving the pores.

This uncertainty makes it difficult to interpret the results in a mechanistic framework. The relative reactivities of the arenes were as expected for electrophilic aromatic substitutions, with toluene more reactive than the halobenzenes. If the rate of diffusion had been determining the reactivity, one would have expected bromobenzene to be as reactive as toluene. This was not the case, indicating the chemical reaction to be the rate determining step. As we have seen, the substitution pattern gave no unambiguous clue to the mechanism, but could be explained by an electrophilic substitution followed by rapid isomerisation.

Conclusions. The results from the two catalysts can be interpreted in a common framework. Over H-ZSM-5, both the reactivities of the five arenes and the substitution patterns indicated the product composition to be determined by the rate of chemical reaction, not by the rate of diffusion. Further, the reaction appears to be of a Friedel-Crafts type with the formation of a Wheland intermediate as the rate determining step.

Over mordenite-H, the results are not that clear. The reactivities were again as expected for electrophilic aromatic substitutions, but the initial substitution patterns were obscured by subsequent isomerisations. The observed substitution patterns together with the results from isomerisation experiments can, however, be interpreted as initial Friedel-Crafts reactions giving normal substitution patterns, followed by rapid isomerisations in the catalyst pores to give product mixtures close to the thermodynamic stable ones.

The results also show that the same type of arenes that are alkylated in Friedel-Crafts reactions in solution can also be alkylated over acidic heterogeneous catalysts. Of the two used in this work, H-ZSM-5 had a longer life time, and also resulted in a high regioselectivity. When a high yield of *para* substituted product is desired this is the catalyst of choice. H-Mordenite had a shorter life time and gave a mixture of the three isomeric alkyl arenes. For a high yield of the *meta* isomer, H-mordenite as catalyst will give a higher yield than what is found for alkylations in solution. It should also be noted that these acidic catalysts are easier handled and disposed of than those normally used in liquid phase alkylations.

EXPERIMENTAL

The experimental set up for the catalysed reactions has been described.¹⁰ The outlet of the reactor was coupled by a valve to a Perkin-Elmer F33 GC equipped with a 2.5 m SP 1200 (5 %) and Bentone (5 %) on 100/200 Supelcoport. GC analyses were possible every 10 min. The mordenite-H was commercially available (Zeolon 200H, Norton Co). and the H-ZSM-5 was prepared as reported.¹¹ New samples of catalysts were used for each experiment. The catalyst was activated at 450 °C for 30 min in a stream of nitrogen before reaction. The aromatic compound was passed into the reactor for 10 min before introduction of ethylene (to avoid polymerisation). The sensitivity of the GC detector towards the components of the reaction mixtures was determined by passing standard mixtures through an empty reactor and into the GC. The identity of the products was checked by GLC/MS analyses of condensed samples of the products (Hewlett-Packard 5985 system). The *meta* and *para* isomers of the ethylhalobenzenes were not separated by the GC. The ratio of these were determined by ¹³C NMR (JEOL FX 100). The NMR spectra were run under non-NOE conditions. The starting materials and products were commercially available except for the isomers of the ethylhalobenzenes. These were prepared by Sandmeyer reactions on the corresponding ethylanilines.

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