A Theoretical Investigation on the Methylation of Methylbenzenes on Zeolites

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Methylation of different methylbenzenes on a zeotype acid catalyst has been investigated through quantum chemical calculations on a cluster model. The activation energy for methylation decreases as the number of methyl groups already in place on the benzene increases. Implications for the mechanism of the methanol-to-hydrocarbon (MTH) reaction are discussed.

1. Introduction

The catalytic conversion of methanol-to-hydrocarbons (MTH) on acidic microporous catalysts such as zeolites and SAPOs has been the subject of a large number of publications.[1,2] The MTH process is a potentially important technology for conversion of natural gas to value-added products, and an improved insight into mechanistic aspects of the MTH reaction is thus desirable. Lately, a mechanism, termed the "hydrocarbon pool" mechanism, in which adsorbed hydrocarbons are methylated by methanol, followed by elimination of the olefinic products, has been proposed.[3–10] Evidence for such a mechanism is accumulating, but the nature of the hydrocarbon pool is presently not entirely clear. Experimental results indicate that it may consist of cyclopentenyl cations [8] or methylated benzenes/benzenium ions.[7–12] There may be a rather facile interconversion between the two groups of compounds.[8]

In an earlier work, we investigated the species inside the pores of a SAPO-34 catalyst during the MTH process experimentally by quenching the reaction and analyzing the pore contents after dissolution of the catalyst material.[11] This approach gives information about the species that are sterically kept from escaping the catalyst during the process. Polymethylbenzenes are the major species found. Experiments have been carried out in which the reactant/carrier gas flow was switched to pure carrier gas a certain time before quenching, to investigate the lifetimes of different confined species. It appears that the most highly methylated benzenes disappear first, followed by the benzenes with fewer methyl groups.[11] Further, experiments in which ordinary and isotopically labeled methanol could be fed intermittently have shown that methanol carbon, besides being found in the methyl groups, may also be incorporated into the benzene rings. Finally, when switching the isotopic composition of the feed, product molecules with the preceding isotope appeared in the olefinic products well after a complete replacement in the unconverted feed in the effluent had taken place. These experiments provide evidence for an active hydrocarbon pool, and that the pool consists of methylated benzenes.

On this background, it is clear that an enhanced insight in (poly)methylbenzene chemistry is of interest for the MTH

chemistry. Methylation by methanol (or dimethyl ether) is a first step in the reaction sequence. Subsequent steps are not considered here. Methylation of, for example, toluene to higher value products is also of interest in itself, although not the main objective for this study.

Until quite recently the number of theoretical works on methylation of aromatics was very limited. Early works, due to lack of computational capacity, were based on semiempirical methods. Two main mechanisms for arene methylation by methanol in acidic zeolites have been proposed in the literature: (1) A sequential mechanism where the methyl group, after methanol protonation and C–O bond rupture, is bonded to a zeolite oxygen. The oxygen-bonded methyl group then attacks the arene. (2) An associative mechanism, where there is concerted attack by the acidic zeolite proton on the methanol oxygen, a simultaneous breaking of the C–O bond in methanol, and formation of a C–C bond between the methyl group and the arene.

Early on, the sequential methylation reaction was usually considered the more likely. Early theoretical work by Corma et al.[13] and Nulen et al.[14] were based on the sequential mechanism. Semiempirical methods were used. Ivanova and Corma later obtained experimental evidence that the reaction is more likely to proceed by the associative mechanism.[15] Blaszkowski and van Santen carried out computations on the associative as well as the sequential mechanism, and concluded that the associative mechanism had the lower activation energy, but in the presence of water, the difference was rather small.[16] The computations were carried out using density functional theory (DFT), but the simplest possible zeolite model: the HOHAl(OH)$_3$ cluster.

During the last year or so, several theoretical works treating methylation by methanol, or methyl group movements as isomerizations and transmethylations have appeared.[17–20] All of these papers use DFT theory. The two papers by Vos et al.,[17,18] which treat toluene methylation with methanol, are of particular relevance relative to this work. They are discussed below.

Our main objective is to obtain further insight into the MTH reaction. We have undertaken quantum chemical calculations of the reaction and activation energies of methylation of three different arenes: methylbenzene, tetramethylbenzene, and hexamethylbenzene. There is experimental evidence that also the

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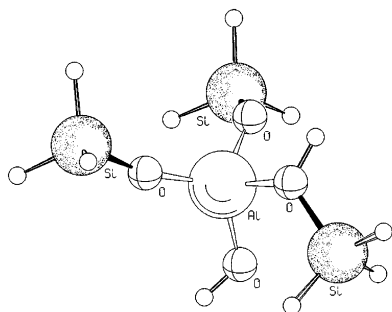*J. Phys. Chem. B, Vol. 106, No. 49, 2002* **12723**

Figure 1. The cluster used as zeolite model.

latter may be further methylated, thereby forming a heptam-ethylbenzenium (ion). The catalytic material is approximated with a cluster (4 T atoms) centered around an acidic site.

2. Computational Details

All calculations were carried out with the Gaussian 98 program.[21] All geometry optimizations were performed using the B3LYP hybrid density functional and 6-31G* basis sets using no geometric constraints. For all transition states, vibrational spectra were calculated to ensure that exactly one imaginary frequency was at hand. Similarly, stable states were checked for the absence of imaginary frequencies. Zero-point energies (ZPE) from these frequency calculations were used for the ZPE-corrected energies reported below. Additionally, single-point energies were calculated at these geometries with the B3LYP/6-311G** and MP2/6-31G* schemes. The zeotype material is modeled by a cluster containing 4 T-atoms, (Figure 1). The systems investigated are far too complex to be handled automatically by the TS keywords. The QST procedures implemented in Gaussian 98 were tried, but failed. Transition states were determined by judiciously optimizing a structure felt by chemical intuition to be close to the transition state, and then optimize for the transition structure with no structural constraints.

3. Results and Discussion

The arenes chosen for methylation are toluene, 1,2,4,5-tetramethylbenzene (henceforth denoted by its trivial name, durene), and hexamethylbenzene (henceforth called hexaMB).

The three reactants are methylated to *p*-xylene, pentamethyl-benzene (pentaMB), and heptamethylbenzenium (heptaMB[+]), respectively. At present the indications are in favor of a concerted associative one-step mechanism rather than a two-step mechanism with methylation via zeolite methoxide.[15,16] We have assumed an associative mechanism. For all reactions, methylbenzene and methanol coadsorbed on the zeolite cluster was taken as the starting point, and this system was structure optimized. Vos et al.[17,18] very recently published studies on methylation of benzene and toluene using the same cluster as we have used, and the functionals B3LYP or MPWPW91, in both cases with 6-31G* basis sets. The methanol molecule is adsorbed on the cluster in the same way in all three cases (end on), but the MPWPW91 functional appears to give slightly smaller hydrogen bond distances than B3LYP.

Figure 2 gives a pictorial representation of the stationary points on the reaction path for methylation of toluene to *p*-xylene as found in this work. From the figures given in the works by Vos et al., it seems that the arene in the adsorbed reaction complex is oriented somewhat differently from what we found, but they do not specify the arene orientation. We have actually found a slightly stronger adsorption than they found using the MPWPW91 functional. We found 90 kJ/mol compared to 88 kJ/mol in their case (ref 17, Figure 8). In the case where they applied the B3LYP functional, they gave only the adsorption energy for the benzene/methanol system, 84.3 kJ/mol (ref 18, Figure 4). Benzene might be less prone to adsorption than methylbenzene, so a direct comparison may not be warranted. All the above values are ZPE-corrected. Apparently, there are several very similar adsorption energy minima. Details on adsorption energies, with and without ZPE corrections, for all three computation schemes used in this work are given in Table 1.

Structural details of the reaction paths for the reactions we have studied are given in Figure 3 and Table 2. Energies of the stationary states are given in Table 1.

At the transition state, the methanol hydroxyl group is almost fully protonated by the acidic proton on the zeolite (OH distance in water is 0.96 Å), $R(O_mC_m)$ is extended to more than 2.2 Å (the CO distance in methanol is 1.4 Å), so the bond is essentially broken, and the CH$_3$ group is essentially cationic, CH$_3^+$. The cationic CH$_3^+$-group is almost planar at the transition state, with the hydrogen atoms slightly bent away from the aromatic species
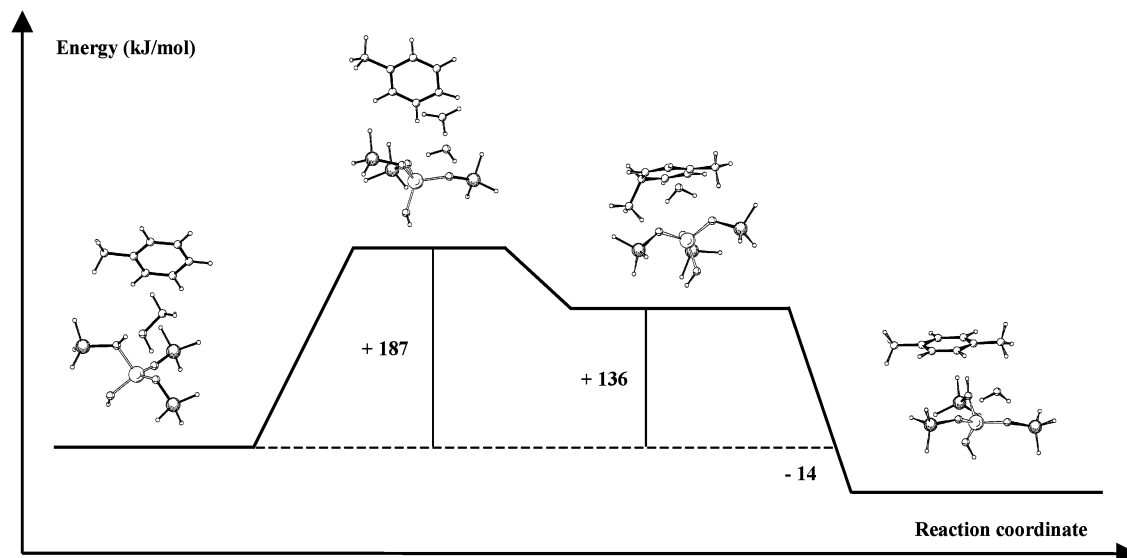

Figure 2. Structures and energies at the B3LYP/6-31G* level of theory for the methylation of toluene to *p*-xylene.

TABLE 1: Stationary Point Energies[a] Relative to the Adsorbed Reactants, with and without ZPE Corrections, for all Computational Schemes Used in This Work[b]

reactants	gas-phase reactants	transition state	protonated products	neutral products	method
		Electronic Energies			
toluene + CH_3OH	106	191	144	−10	B3LYP/6-31G*
	95	195	148	−25	B3LYP/6-311G**
	127	194	137	−45	MP2/6-31G*
durene + CH_3OH	105	174	122	8	B3LYP/6-31G*
	90	169	124	−13	B3LYP/6-311G**
	128	169	102	−33	MP2/6-31G*
hexaMB + CH_3OH	106	171	106		B3LYP/6-31G*
	83	154	92		B3LYP/6-311G**
	134	158	85		MP2/6-31G*
		B3LYP/6-31G* Energies, including ZPE Corrections			
toluene + CH_3OH	90	187	136	−14	B3LYP/6-31G*
durene + CH_3OH	90	171	121	7	B3LYP/6-31G*
hexaMB + CH_3OH	89	169	108		B3LYP/6-31G*

[a] Values are in kJ/mol. [b] All geometries are obtained using B3LYP/6-31G*. The level of theory, the energies are calculated at, are shown in the table.

TABLE 2: The Most Important Transition State Bond Lengths (Å) in the Studied Reactions[a,b]

	toluene	durene	hexamb	toluene[c]	toluene[d]
$R(O_1H_1)$	1.936	1.856	1.863	1.899	1.84
$R(O_2H_2)$	1.834	1.819	1.813	1.874	1.81
$R(H_1O_m)$	0.983	0.986	0.986	0.985	1.00
$R(H_2O_m)$	0.988	0.988	0.989		
$R(O_wC_m)$	2.266	2.228	2.216	2.281	2.25
$R(C_mC_{ring})$	2.014	2.036	2.076	1.998	1.98
$R(AlC_m)$	3.768	3.959	3.989	3.467	3.45
$R(H_{ring}C_{ring})$	1.088	1.089	−[e]	1.093	1.10
$A°(O_mC_mC_{ring})$	173.4	178.2	176.3	171	170.5
dihedral-CH_3	- 14.5	- 13.8	- 12.8	- 14.57	- 14.5

[a] See Figure 3 for the definitions of the bond names. [b] Missing numbers were not given. [c] Ref 18. Level of theory: B3LYP/6-31G*. The same zeolite model as here. [d] Ref 17. Level of theory: MPWPW91/6-31G*. The same zeolite model as here. [e] There is no hydrogen bonded to the ring. The bond length to the "old" methyl group is 1.527 Å.
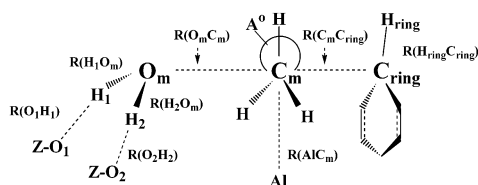

Figure 3. Schematic presentation of the most important geometric parameters in the transition state structures. Z−O indicates an O-atom attached to the zeolite model. In the studied reactions, the most important contribution to the normal mode corresponding to the transition state is along the $O_w−C_m−C_{ring}$ axis. The number of methyl groups on the arenes is not indicated in this figure. Table 2 lists the values of the quantities defined in the figure.

and toward the forming water molecule. A cationic methylbenzene with one more methyl group is thus being formed. The CH_3^+-group undergoes an umbrella-type inversion as the reactants are transformed into products.

In all cases, the aromatic structures are only slightly distorted at the transition state. The aromatic carbon atom (C_{ring}) to which the CH_3^+ group is attaching itself is only slightly displaced from the aromatic plane. The distance between the carbon atom of the CH_3^+ group (C_m) and the aromatic carbon that is being methylated (C_{ring}), increases with an increasing number of methyl groups already attached to the ring, while the distance between O_m and C_m shows an opposite tendency, as seen from Table 2. This is in agreement with general experience in organic chemistry: Alkyl group substituents induce an enhanced electron-donating tendency.

Two of the resulting structures, H^+−p-xylene and H^+−pentaMB, are protonated. They represent stable structures. Vibrational spectra calculations gave zero imaginary frequencies. This is somewhat surprising since it is often stated that stable charged intermediates do not exist.[18] They are described as transition-state structures. However, when Vos et al.[17] carried out a theoretical study of methylation of toluene to p-xylene in mordenite using periodic DFT, they suggested that a charged p-xylene/water complex is a stable structure in the mordenite framework. Also, in our case, water is present and may represent a stabilizing factor even in a small cluster model. (If an arene is methylated by methanol there is always water present.)

We have not found a transition state for the process where the proton is transferred back to a oxygen on the cluster, but expect the barrier for rotating the arene so that the proton comes on the side turned toward the cluster to be very low. Attempts at finding a stable protonated p-xylene with no water present have so far failed. The charged arene appears to form a C−O bond with the cluster.

In the final step, the protons on both xylene and pentaMB are transferred to the cluster zeolite model. After methylation of hexaMB, heptamethylbenzenium cation (heptaMB$^+$) is formed. This species has no protons on the aromatic ring, and hence deprotonation is much less facile. It is known, however, that the methyl group in para position to the gem dimethyl group can shed one of its hydrogens as a proton under formation of an exocyclic double bond (4-methylene-1,1,2,3,5,6-hexamethylcyclohexadiene-2,5).[22]

The fact that heptaMB$^+$ is not aromatic is borne out by the C−C bond distances in the ring. The bond lengths between the carbon with gem dimethyl groups and its two nearest C_{ring} neighbors are calculated to be 1.51 Å. The $C_{ring}−C_{ring}$ bond length between the ring atoms ortho and meta to the gem dimethyl carbon is 1.38 Å, and the two $C_{ring}−C_{ring}$ bond lengths in a position para to the gem dimethyl groups are 1.43 Å. Interestingly, the bond lengths to the two methyl groups on the 4-coordinated C_{ring}-atom is 1.57 Å, which is longer than the 1.51 Å found for methyl groups on all the other ring carbons, and also longer than the "normal" sp^3 hybridization bond length of 1.54 Å. This might be an origin of increased reactivity.

Activation and reaction energies can be found in Table 1. On the basis of experimental work, it has been stated that arene methylation has an apparent activation energy of ca. 50−90 kJ/mol, which is less than what we find in the calculations.[23] However, this discrepancy may safely be ascribed to the cluster

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approximation which severely overestimates the activation energy.[17,19] On the other hand, an apparent activation energy where reactant adsorption enthalpies are ignored underestimates true activation energy. To investigate the adequacy of the method in use, we have carried out energy calculations for the B3LYP/6-31G* geometries at the B3LYP/6-311G** and MP2/6-31G* levels of theory. Gratifyingly, the energy trends are unaffected by the choice of method, indicating that the B3LYP/6-31G* is sufficient for describing energy trends in systems such as the ones under study. At the same time, the disparity of the energies obtained by the different levels of theory indicate that it will probably be necessary to go to a higher level of theory in order to get more precise energies.

The transition state energies for further methylation are seen to become lower as the number of methyl groups already in place increases. Under the assumption that later reaction steps are not too fast, this should indicate that once benzenes are subject to surplus methanol, they would likely be fully methylated until becoming heptaMB$^+$ on the catalyst. This is supported by the recent experimental observation of heptaMB$^+$ on a H−BEA catalyst.[23]

In the present calculations, steric effects of the zeolite framework are not considered. In an experimental case, steric constraints might impose difficulties in the methylation when the aromatic species have many methyl groups. In a small-pore catalyst, the formation of heptamethylbenzenium may be restricted, and in such cases, the hydrocarbon pool might consist of less methylated benzenes. By using space-filling crystal models and docking heptaMB$^+$ ions, we have made certain that in, for example, SAPO-34 there is ample space. In experimental work, we have observed molecules as large as tetramethylnaphthalene, pyrene, and methylpyrene inside the SAPO-34 framework (unpublished).

To obtain fully satisfactory information from quantum chemical calculations it will certainly be necessary to work with more realistic zeolite models. The work carried out by Vos et al.[17] where they utilized a true unit cell of mordenite represents an important step in that direction. Unfortunately, it seems that one is presently restricted to zeolite systems with rather small unit cells, otherwise the computations become too time-consuming. It also appears that one is forced to rely on simplified zeolite models, such as a cluster as used here, as a starting point. A fully rigorous determination of the transition state appears presently to be too demanding, unless one is working with quite simple reaction systems. These difficulties would be further accentuated for the more complex reaction systems treated here. Despite the shortcomings of the cluster models, they may still be very useful. Rozanska et al., when comparing periodic systems with cluster models have found that the cluster model dramatically overestimates activation energies. On the other hand, they report that the cluster model conserves the relative order of activation energies; so approximating the zeolite with a cluster may still be useful for qualitative comparative reactivity studies as done here.[19]

The particular importance of hexaMB in the MTH reaction has been clear for some time.[11,12] This work was undertaken because we felt that the experimental results obtained when switching between ^{13}C and ^{12}C methanol during the MTH reaction over SAPO-34 could not be satisfactorily explained unless hexaMB could be further methylated. The possibility of forming heptaMB ions was known from the experiments of von Doering et al. over Friedel−Crafts methylation of arenes.[22] It is, however, only very recently that experimental evidence for existence of heptaMB in zeolites was obtained.[24] The possibility

of forming this compound in zeolites was therefore an important issue in connection with MTH chemistry. It is now clear that heptaMB is formed as easily as other methylbenzenes if there are no particular spatial restrictions.

Methylation of methylbenzenes appears to be an important step in the MTH reaction. From the present results, and from earlier experimental data, it is very likely that the MTH mechanism goes via a heptamethylbenzenium cation if the catalyst pores can accommodate it. The further role of this cation in the MTH mechanism is not fully understood. It might eliminate smaller hydrocarbons directly, or after further neutralization and methylation. Work along these lines is in progress.

4. Conclusions

We have shown that methylation of methylbenzenes on a zeolitic acid site becomes easier as the number of methyl groups on the benzene ring increases—transition state energies in the methylations of methylbenzenes decrease with increasing number of methyl groups on the benzene ring. The trend is clear, and shows that without steric constraints, formation of heptamethylbenzenium ions is likely. Our results strongly suggest that this ion plays an important role in the MTH mechanism.

The energy trends appear to be rather insensitive to the choice of method, and the B3LYP/6-31G* scheme appears to be sufficient for studies of energy trends for systems such as the one under study, even if the accuracy in the activation and reaction energies themselves leave something to be desired.

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