

KINETIC AND THEORETICAL STUDY OF THE EFFECT OF MOLECULAR SIEVE STRUCTURE ON THE SELECTIVITY TO PROPYLBENZENES IN ALKYLATION OF BENZENE WITH ISOPROPYL ALCOHOL

Jiri CEJKA¹, Nadezda ZILKOVA², Judit E. SPONER³ and Blanka WICHTERLOVA⁴

J. Heyrovsky Institute of Physical Chemistry, Academy of Sciences of the Czech Republic, 182 23 Prague 8, Czech Republic; e-mail: ¹cejka@jh-inst.cas.cz, ²zilkova@jh-inst.cas.cz, ³molnar@jh-inst.cas.cz, ⁴wichterl@jh-inst.cas.cz

Received August 9, 1998
Accepted September 9, 1998

The alkylation of benzene with isopropyl alcohol was investigated over molecular sieves of different structural types and acidity by kinetic measurements and *ab initio* quantum chemical calculations. The formation of n-propylbenzene occurring *via* bimolecular transalkylation between isopropylbenzene and benzene is enhanced by the appropriate geometry of the reaction space and the acidity of molecular sieves. n-Propylbenzene was formed over medium and large pore molecular sieves with such inner channel architecture which enables the approach of isopropylbenzene and benzene to form the reaction complex. Mesoporous sieves of MCM-41 structure provided only isopropylbenzene with some amount of diisopropylbenzenes. For the fully relaxed complex consisting of protonated isopropylbenzene and benzene, the computations verified the transfer of propyl group from one benzene molecule to another forming again isopropylbenzene. When the geometrical conditions modelling the channel intersections of ZSM-5 and ZSM-11 structures were considered n-propylbenzene was formed. The anti-Markovnikov type of proton transfer from the arenium cation to the propene part of the complex is promoted by the steric constraints present in the channel intersections of ZSM-5 and ZSM-11 zeolites.

Key words: Alkylation of benzene; Isopropyl alcohol; n-Propylbenzene formation; *Ab initio* calculation; anti-Markovnikov rule; Zeolites; Molecular sieves; Heterogeneous catalysis.

Aluminium trichloride or supported phosphoric acid on silica are still used as catalysts for the large-scale production of various alkylaromatic hydrocarbons despite severe environmental problems connected to both corrosion of the processing units and the disposal of spent catalysts. The replacement of these catalysts by more environment-friendly ones, exhibiting, moreover higher activities and selectivities is one of the challenges in heterogeneous catalysis, which could be reached taking advantage of zeolite-based catalysts.

Molecular sieves^{1,2} are well-known to exhibit high activity and selectivity in acid catalyzed transformations of hydrocarbons. These reactions proceed almost exclusively in the inner channel system of zeolites bearing acid sites and, thus, their activities and selectivities are strongly affected not only by their acidic properties but also by the size

of the inner volume available for the catalytic reaction. The so-called *shape selectivity*³⁻⁶ originates from transport limitations of reactants and products in/out the channels, and/or in formation of bulky intermediates (*restricted transition-state shape-selectivity*). Recently we have found another type of the transition-state shape-selectivity (*structure-directed transition-state selectivity*) operating if proper geometry and architecture of the zeolite channel system induce formation of an intermediate complex not formed in a non-restricted reaction volume⁶⁻⁹.

Isopropylbenzene (cumene) is a starting material for the production of phenol, acetone and α -methylstyrene and thus belongs to a family of chemical commodities with a large production. During the last decade, new processes of benzene alkylation with propene catalyzed by molecular sieves were introduced by Dow Chemical-Kellog, Mobil-Badger, ABB Lummus Global, and EniChem¹⁰⁻¹³ based on dealuminated mordenite or Beta zeolite. However, on these catalysts, small concentrations of undesired n-propylbenzene and diisopropylbenzenes are formed. It was found that low selectivity to n-propylbenzene can be usually attained over large-pore zeolites, which, however, have some tendency to form diisopropylbenzenes and also to deactivate in time-on-stream. On the other hand, medium-pore zeolites with three-dimensional channel system of intersecting channels, though more resistant to deactivation, yield n-propylbenzene in a non-negligible amount¹⁴⁻²⁰. This led us to the investigation of the mechanism of n-propylbenzene formation.

On the basis of kinetic investigations, it was suggested that the rate determining step of benzene alkylation with isopropyl alcohol is desorption and transport of bulky, strongly adsorbed propylbenzene molecules if the reaction takes place in gaseous phase at about 520 K. As for the mechanism of n-propylbenzene formation, Fraenkel and Levy¹⁵ originally assumed that n-propylbenzene is produced *via* monomolecular isomerization of isopropylbenzene formed in the alkylation step. Beyer and Borbely²¹ observed n-propylbenzene in the products only if an excess of benzene was present in the reaction mixture. The mechanism of n-propylbenzene formation was finally elucidated by the experiments with labeled propene as alkylating agent for benzene alkylation over ZSM-11 (refs^{16,18}) and by the transalkylation reaction between 4-isopropylmethylbenzene and benzene over ZSM-5 (refs^{7,8}) leading to the formation of n-propylbenzene. These experiments proved that n-propylbenzene is formed *via* the bimolecular transalkylation between isopropylbenzene and benzene which takes place only in a restricted reaction volume of certain molecular sieve structures.

Ab initio quantum chemical calculations provide a theoretical approach to investigation of reaction mechanisms of transformations of various organic molecules over molecular sieves, to distinguishing individual reaction steps, and to characterization of transition states and reaction intermediates. Numerous examples can be found in the literature, *e.g.* in papers of Blaszkowski and van Santen or of Corma's groups²²⁻²⁶. These calculations discussed the elementary steps of the methanol-to-gasoline process

or the skeletal isomerization of butane and n-butene to 2-methylpropane and 2-methylpropene, respectively.

This contribution provides a more general view on the mechanism of the alkylation of benzene with isopropyl alcohol centred on the conditions required for the formation of isopropyl- and n-propylbenzenes. A set of molecular sieves of various structures and strength and concentration of acid sites was investigated. The experimental and theoretical considerations of the mechanism of n-propylbenzene formation are presented. In the theoretical part of this study, we assumed that the reaction complex can be sufficiently described by a complex consisting of protonated isopropylbenzene and benzene, the first step of its formation being proton transfer from the zeolite bridging OH group to the isopropylbenzene molecule. Mass spectrometric and *ab initio* studies^{27,28} have shown that the protonated isopropylbenzene molecules can be stabilized in two ion-molecule complexes depending on the location of the attached proton. The complex $[C_6H_7^+ \cdot C_3H_6]$ was chosen as the appropriate model for the description of protonated isopropylbenzene. Because the experimental results have shown that the formation of n-propylbenzene proceeds *via* bimolecular reaction and depends primarily on the steric hindrances of the individual molecular sieves used, the calculations were carried out in two steps. Firstly, a full optimization was performed on the structure of the complex of cation $[C_6H_7^+ \cdot C_3H_6]$ with a reactant benzene molecule, and secondly the steric hindrances simulating the perpendicularity of the channels of ZSM-5 and ZSM-11 structures were used.

EXPERIMENTAL

Molecular Sieves

Acid form of H-(Al)ZSM-5 zeolite with Si/Al ratio of 22.5 was prepared using an acid solution treatment (0.5 M HNO_3 , 298 K) of the parent Na-zeolite (purchased from the Institute for Oil and Hydrocarbons Gases, Bratislava, Slovak Republic). The synthesis of ferrisilicate of MFI structure [H-(Fe)ZSM-5] has been described elsewhere¹⁹. An analogous procedure was employed for the synthesis of H-(Al)ZSM-11 and H-(Fe)ZSM-11 but tetrabutylammonium hydroxide was used instead of tetrapropylammonium hydroxide. The synthesis of H-(Al)ZSM-12 and H-(Fe)ZSM-12 was performed with triethylmethylammonium bromide as structure-directing agent according to ref.²⁹ with the exception that aluminium nitrate was substituted for ferric nitrate. ZSM-23 was synthesized according to the procedure kindly provided by Dr S. Ernst³⁰ using Cab-O-Sil M5, sodium hydroxide, aluminium sulfate and pyrrolidine. NH_4 -Y zeolite with Si/Al ratio of 2.5 and NH_4 -mordenite (H-M) with Si/Al ratio of 7.3 were supplied by the Research Institute for Oil and Hydrocarbon Gases (Bratislava, Slovak Republic). Zeolite H-Beta (Si/Al = 12.5) was purchased from PQ Corporation (U.S.A.).

Aluminophosphate molecular sieve CoAlPO-5 was prepared modifying the synthesis procedure described in ref.³¹ using cobalt acetate as a source of cobalt and tetraethylammonium hydroxide as template.

The synthesis of aluminium-containing mesoporous molecular sieve MCM-41 was carried out in our laboratory using modified procedure described in ref.³² with hexadecyltrimethylammonium hydroxide, Cab-O-Sil M5, sodium silicate, tetramethylammonium hydroxide and sodium aluminate.

All the synthesized molecular sieves were calcined in a stream of air at 820 K for 6 h to remove the organic template. Their ammonium forms were prepared by a repeated ion-exchange with 0.5 M ammonium nitrate at ambient temperature.

The concentration of heteroatoms in the molecular sieves was determined, after their dissolution, by atomic absorption spectrometry. The proportion of heteroatoms located in the framework sites was estimated from temperature-programmed desorption of ammonia and the NH_4^+ ion-exchange capacity. It has been found that aluminium-containing molecular sieves were almost free of extra-framework Al species (<1.5%), in the case of iron-containing analogues about 10% of iron species were located in the extra-framework positions.

Characterization of Catalysts

The molecular sieves used were checked by X-ray powder diffraction (Seifert 3000P), scanning electron microscopy (JEOL), and FTIR spectroscopy (Nicolet Magna-550) to confirm their high crystallinity and phase purity.

Concentration of the bridging OH groups was determined from the high-temperature peak of the temperature-programmed desorption of ammonia (performed in a helium stream from 373 up to 823 K) and from the intensity of IR bands of bridging OH groups and of adsorbed d_3 -acetonitrile. The details of these procedures are given elsewhere¹⁷, for estimation of corresponding extinction coefficients see ref.³³.

Benzene Alkylation with Isopropyl Alcohol

The alkylation of benzene with isopropyl alcohol was performed in a down-flow microreactor (inner diameter of 10 mm, weight of dry catalyst 0.40 g, grain size 0.3–0.6 mm) at 520 K and WHSV 10 h^{-1} . A nitrogen stream was saturated with an equilibrium concentration of benzene at 316 K to a level of 18.5 vol.% and mixed with another stream of nitrogen equilibrated with isopropyl alcohol (at 308 K) to reach the benzene/isopropyl alcohol molar ratio 9.6 in the final reactant mixture. The reaction products were analyzed using an "on-line" gas chromatograph (Hewlett–Packard 5890 Series II) equipped with a high-resolution capillary column SUPELCOWAX 10 (30 m length, i.d. of 0.2 mm, phase thickness 0.2 μm) and with the flame ionization and mass spectrometric (Hewlett–Packard 5971A) detectors.

Ab initio Quantum Chemical Calculations

Geometries of all complexes were optimized within the Hartree–Fock (HF) approximation with the 6-31G** basis set of atomic orbitals. Analytic gradients have been computed following the Berny algorithm. In several cases analytic second derivatives had to be used to obtain optimized structures. We studied initial and final structures of the transalkylation and transalkylation/isomerization reactions of complex $[\text{C}_6\text{H}_7^+-\text{C}_3\text{H}_6-\text{C}_6\text{H}_6]$ leading to isopropyl- and n-propylbenzenes and a number of structures where the C...H distance was fixed along the proposed reaction pathway.

To estimate the effect of dispersion energy on the intermolecular stabilization of various complexes the intermolecular energies were evaluated using the second-order Møller–Plesset (MP2) perturbation theory. Standard 6-31G basis set augmented by one set of diffuse (momentum-optimized; exponent of 0.25) d-polarization functions was used. These calculations were made as single-point energy calculations using the HF/6-31G** optimized geometries which is abbreviated as MP2/6-31G* (0.25)/HF/6-31G** level. All *ab initio* quantum chemical calculations were carried out using the Gaussian 94 computer code. The details of the calculation procedure are given elsewhere³⁴.

RESULTS AND DISCUSSION

As this contribution is focused on the explanation of the effect of the architecture of the inner zeolite channels on the formation of *n*-propylbenzene in the benzene alkylation with isopropyl alcohol, Tables I and II summarize only benzene conversion, selectivity to propylbenzenes, and isopropyl/*n*-propylbenzene ratio. Detailed product composition for some zeolites can be found in refs^{7,8}.

Molecular Sieves with One-Dimensional Channel System

Table I gives the results of benzene alkylation with isopropyl alcohol for molecular sieves possessing one-dimensional channel system differing in the dimensions of their channels, *i.e.* medium-pore, large-pore and mesoporous systems.

No *n*-propylbenzene was observed for medium-pore H-(Al)ZSM-23 zeolite. For one-dimensional large-pore zeolites, namely H-(Fe)ZSM-12, H-mordenite (second eight-member channel ring is too small to accommodate benzene molecules) and CoAlPO-5 again no *n*-propylbenzene was produced and only traces of *n*-propylbenzene were found over H-(Al)ZSM-12 (Table I). These results are in agreement with the proposed bimolecular mechanism considering the formation of the large 1,2-diphenylpropane intermediate which is too bulky to fit into the one-dimensional channel systems of these molecular sieves^{7,16}. However, with MCM-41 possessing wide one-dimensional channels (about 35 Å), *n*-propylbenzene was not formed either, although the inner volume was sufficient to accommodate this bulky intermediate complex. The only observed products over MCM-41 were isopropylbenzene and all three isomers of diisopropylbenzenes (Table I).

The results obtained over one-dimensional molecular sieves clearly showed that the formation of *n*-propylbenzene does not depend on the reaction space available but on the architecture of the reaction volume. *n*-Propylbenzene is not formed over medium- and large-pore zeolites where 1,2-diphenylpropane intermediate cannot be accommodated for steric reasons, but it is also not formed over mesoporous MCM-41 with significantly larger pores.

Molecular Sieves with Three-Dimensional Channel System

A substantially different product composition was observed for three-dimensional channel systems represented by medium-pore H-(Al) and H-(Fe)ZSM-5, and H-(Al) and H-(Fe)ZSM-11 molecular sieves, and large-pore H-Y zeolite and H-Beta (Table II). A small amount of *n*-propylbenzene is formed over H-Y zeolite. Zeolite Y is able to accommodate in its large cavity also 1,1-diphenylpropane complex, which is probably more energetically favoured, and is further transformed again into isopropylbenzene and benzene. This means that only transalkylation of isopropyl group from one benzene

TABLE I

Concentration of strong acid OH groups, channel dimensions, and activity and selectivity in benzene alkylation with isopropyl alcohol for molecular sieves with one-dimensional channel system (time-on-stream 95 min)

Zeolite	H-(Al)ZSM-12	H-(Fe)ZSM-12	H-Mordenite	CoAlPO-5	MCM-41A	MCM-41B
OH groups, mmol/g	0.16	0.34	1.48	0.6 ^b	1.03 ^c	0.74 ^c
Channel dimensions, Å	5.5 × 5.9	5.5 × 5.9	6.5 × 7.0	7.3	35	35
Benzene conversion, %	4.4	4.9	7.0 ^a	5.6	6.2	5.2
Propylbenzenes, mole %	92.5	96.4	93.8	92.1	80.2	83.4
Isopropyl-/n-propylbenzene ratio	103.7	∞	∞	∞	∞	∞

^a Time-on-stream 15 min; ^b mmol Co/g; ^c mmol Al/g.

TABLE II

Concentration of strong acid OH groups, channel dimensions, and activity and selectivity in benzene alkylation with isopropyl alcohol for molecular sieves with three-dimensional channel system (time-on-stream 95 min)

Zeolite	H-(Al)ZSM-5	H-(Fe)ZSM-5	H-(Al)ZSM-11	H-(Fe)ZSM-11	H-Beta	H-Y
OH groups, mmol/g	0.69	0.54	0.41	0.42	1.05	4.30
Channel dimensions, Å	5.3 × 5.6 5.1 × 5.5	5.3 × 5.6 5.1 × 5.5	5.3 × 5.4	5.3 × 5.4	7.6 × 6.4 5.5 × 5.5	7.4
Benzene conversion, %	6.2	8.6	5.3	6.7	8.6	8.7
Propylbenzenes, mole %	87.9	97.1	89.2	95.6	88.7	89.8
Isopropyl-/n-propylbenzene ratio	7.6	45.9	9.1	55.3	23.4	93.4

ring to another benzene molecule proceeds, however, not accompanied by isomerization of isopropyl group to n-propyl one. A significantly higher concentration of n-propylbenzene was obtained with large-pore zeolite H-Beta possessing three-dimensional channel system with intersecting channels without large cavities. The highest selectivity to n-propylbenzene was reached using medium-pore zeolites H-(Al)ZSM-5 and H-(Al)ZSM-11 (Table II). For isomorphously substituted (Al) and (Fe)ZSM-5 and ZSM-11 the overall conversion of benzene is governed by desorption and transport of bulky products while the rate of transalkylation or transalkylation/isomerization reactions is controlled by the acid strength of bridging OH groups. The higher the acid strength of bridging OH groups ($\text{Si-OH-Al} > \text{Si-OH-Fe}$), the higher the rate of the transalkylation/isomerization reaction leading to the formation of n-propylbenzene.

It follows that n-propylbenzene is formed almost exclusively over H-ZSM-5, H-ZSM-11 and H-Beta. Thus, for elucidation of the role of the zeolite architecture in this reaction, the similarity among ZSM-5, ZSM-11 and Beta structures should be considered. These structures are three-dimensional with intersecting channels without large cavities; moreover, the dimension of channel of zeolite Beta along the [001] axis is comparable with the dimensions of ZSM-5 and ZSM-11 channels.

Ab initio Quantum Chemical Calculations of the Transalkylation Between Isopropylbenzene and Benzene

Ab initio quantum chemical calculations have been used to describe the possible reaction pathways of n-propylbenzene formation both for restricted and non-restricted reaction volume. The monomolecular isomerization of isopropylbenzene to n-propylbenzene has been ruled out by Berthomieu *et al.*^{27,28} because of higher thermodynamic stability of the protonated isopropylbenzene compared to the n-propylbenzene carbocations. On the other hand, it has been shown that protonated n-propylbenzene can irreversibly isomerize to protonated isopropylbenzene prior to dissociation³⁵.

Experimental data provide an evidence that bimolecular reaction proceeds in medium-pore zeolites with three-dimensional channel system and it was suggested that particularly the intersections in ZSM-5 and ZSM-11 channel structures are appropriate reaction volume for intermediate complex formation. To evaluate the role of the zeolite structure in the transalkylation reaction, the restricted reaction volume was simulated by fixing the perpendicularity of the benzene rings of the reaction complex (described as $[\text{C}_6\text{H}_7^+-\text{C}_3\text{H}_6-\text{C}_6\text{H}_6]$). The energy profiles of the reactions in restricted and non-restricted reaction volume are presented in Fig. 1. The horizontal axis represents the reaction coordinate (τ), *i.e.*, the distance between the $\text{C}(\text{sp}^3)$ carbon of the benzenium cation and the bridging H atom. The dotted line depicts the curve obtained for non-restricted, fully optimized, and the solid one for restricted reaction volume. The individual reaction complexes (structures 1–7) are presented in Fig. 2.

When no sterical restrictions are considered, transfer of isopropyl group from one benzene ring to the other takes place. In the initial state complex (structure **1**), the protonated benzene ring points towards the non-protonated benzene ring (representing the reactant benzene molecule). The propene part and the benzenium cation are linked together *via* a hydrogen bond. The isopropyl group is generated *via* Markovnikov type proton transfer from the C(sp³) carbon of the benzenium cation to the primary carbon of propene moiety (the proton involved in the transfer is indicated by • in all the struc-

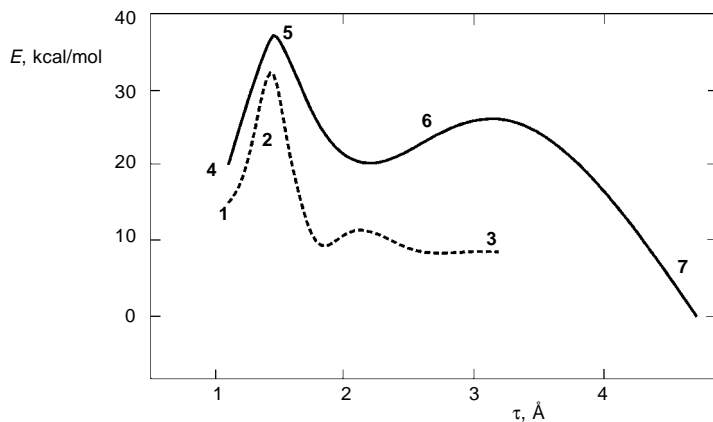


FIG. 1

Computed energy profiles of the bimolecular transalkylation reaction between protonated isopropylbenzene and benzene (--- non-restricted reaction volume, — restricted reaction volume). The numbers belong to the structures depicted in Fig. 2

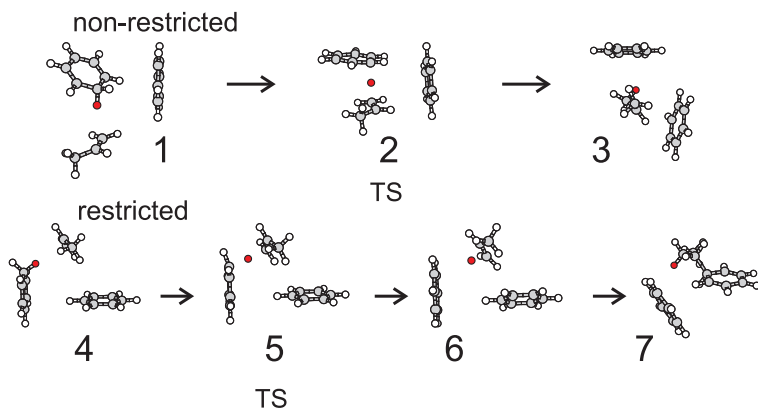


FIG. 2

Representative structures along the computed reaction pathways for restricted and non-restricted reaction volume (TS transition state, for the numbering of the structures, see Fig. 1)

tures). The rate determining step of this reaction is the cleavage of the C(sp³)-H bond requiring an activation energy of 17 kcal/mol. In the transition state complex the transferred proton is stabilized by an interaction with the propene and benzene molecules (see structure **2**). The step-by-step displacement of the proton from benzenium cation towards the propene part of the complex is accompanied by a shift of the reactant benzene molecule towards the secondary carbon of the propene part promoting the Markovnikov type proton addition. At the destination, illustrated by structure **3**, the secondary carbon of the isopropyl carbocation holds the positive charge pointing to the center of the reactant benzene molecule. This interaction leads to an enormous stabilization of the complex (computed intermolecular interaction energy between these two parts is -14.4 kcal/mol). It should be noted that the complex of the isopropyl cation with the reactant benzene molecule [C₆H₆·C₃H₇⁺] (structure **3**) closely resembles the more energetically favoured ion-molecule structure suggested by Berthomieu *et al.*²⁷.

Completely different results were obtained when the perpendicularity of the benzene rings in the initial complex was fixed. From the comparison of structures **4** and **5** it can be seen that the proton transfer does not involve substantial changes in the global structure of the reaction complex, owing to the restriction on the mutual position of the benzene rings. The rate determining step of the reaction is again the cleavage of the C(sp³)-H bond with the same activation energy of 17 kcal/mol. Nevertheless, a substantial structural difference between the two transition state complexes has to be stressed emerging from the average interatomic C-C distances, measured between the nearest carbon atom of the reactant benzene ring and the primary or secondary carbons of the propene. In the transition state complex obtained for non-restricted reaction volume (structure **2**) both the primary and secondary carbon atoms of the propene moiety are accessible to the protonation while in the restricted reaction volume (structure **5**) the secondary carbon is preferred following, thus, the anti-Markovnikov rule. In line with this, in addition to the Markovnikov type an anti-Markovnikov type pathway has been found, the latter being responsible for the n-propylbenzene formation. Structure **6** corresponds to the reaction complex with proton in the bridging position over the double bond of the propene part. The energy of this structure is by 13.2 kcal/mol lower than that of the transition state complex indicating that the anti-Markovnikov type pathway does not require investment of extra energy. This can be evidently attributed to the effect of the interacting benzene rings, that stabilizes the transient cationic center on the primary carbon of the propene part in structure **6**. The final stabilization of the n-propyl group formed according to anti-Markovnikov type proton transfer is achieved *via* formation of the chemical bond between the n-propyl group and the reactant benzene molecule. Thus, the thermodynamic stability of the anti-Markovnikov type product depicted by structure **7** – a complex of protonated n-propylbenzene and benzene – is by 20 kcal/mol higher than that of the initial state complex. This significant stabilization

of the product can provide an explanation why the anti-Markovnikov type pathway becomes preferred.

By examining the steric dimensions of the reaction complex obtained with geometrical constraints we have found an explanation of the experimental finding, *i.e.* that the optimum reaction space for the transalkylation/isomerization reaction is provided by the ZSM-5 and ZSM-11 zeolite structures. This optimum reaction space was obtained by fixing the perpendicularity of both benzene rings as assumed for intersections of ZSM-5 and ZSM-11 structures. Figure 3a depicts the reaction complex embedded in the ZSM-5 structure. For comparison, the same complex accommodated in zeolite Beta is shown in Fig. 3b. It can be seen, that the optimum reaction volume is given by the ZSM-5 channels, because the reaction complex completely fills the available reaction space. In contrast, there is more space to accommodate the reaction complex in the channels of the Beta structure, which results in the lowering of the selectivity to *n*-propylbenzene compared to that measured over ZSM-5 and ZSM-11 structures.

CONCLUSIONS

The formation of *n*-propylbenzene in the transalkylation step is significantly influenced by the acidity of the active sites of zeolites (both strength and concentration of protonic sites) but primarily by the proper channel architecture and dimensions of perpendicularly oriented channels. Formation of bimolecular intermediate complex is sterically hindered in the one-dimensional channel system of medium- or large-pore zeolites [H-(Al)ZSM-23, CoAlPO-5, H-mordenite, H-(Al)ZSM-12, H-(Fe)ZSM-12]. The catalytic experiments carried out with different structural types of molecular sieves confirmed that the formation of *n*-propylbenzene is directed by the appropriate structure of zeolites ZSM-5 and ZSM-11.

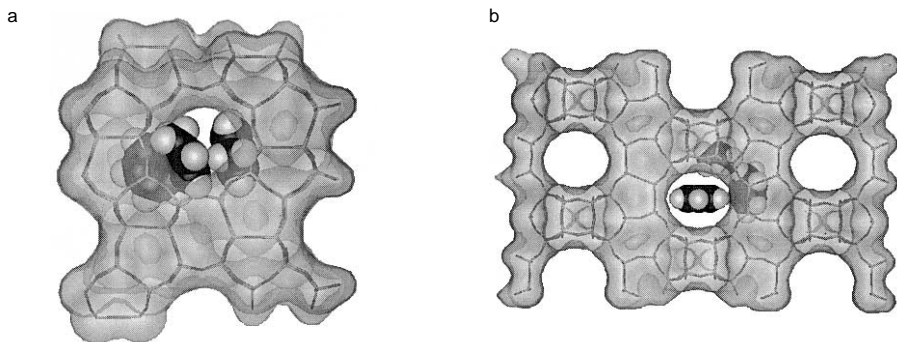


FIG. 3

Steric conditions for the accommodation of the initial state complex in the ZSM-5 and Beta structures (a ZSM-5, view along the [100] axis; b Beta, view along the [100] axis)

Ab initio quantum chemical calculations have shown that the primary product of the reaction between protonated isopropylbenzene and benzene in restricted reaction volume (simulating ZSM-5 and ZSM-11 structures) is a complex of protonated n-propylbenzene and benzene.

The bimolecular isomerization reaction is initiated by the transfer of the bridging hydrogen from the sp^3 carbon of the benzenium moiety towards the propene part. The anti-Markovnikov type proton addition to the propene part is promoted by the formation of a covalent bond between the reactant benzene molecule and the propene moiety resulting in a substantial stabilization of the complex.

Financial support from the Grant Agency of the Academy of Sciences of the Czech Republic (grant No. A4040707) is highly acknowledged.

REFERENCES

1. a) Szostak R.: *Molecular Sieves*. Blackie Acad. & Prof., New York 1998; b) Szostak R.: *Handbook of Molecular Sieves*. Van Nostrand Reinhold, New York 1992.
2. a) Cundy C. S.: *Collect. Czech. Chem. Commun.* **1998**, *63*, 1699; b) Sheldon R. A., Arends I. W. C. E., Lempers H. E. B.: *Collect. Czech. Chem. Commun.* **1998**, *63*, 1724.
3. Weisz P. B.: *Pure Appl. Chem.* **1980**, *52*, 2091.
4. Csicsery S. M.: *Zeolites* **1984**, *4*, 202.
5. Csicsery S. M.: *Pure Appl. Chem.* **1986**, *58*, 841.
6. Mirth G., Cejka J., Lercher J. A.: *J. Catal.* **1993**, *139*, 24.
7. Wichterlova B., Cejka J.: *J. Catal.* **1994**, *146*, 532.
8. Wichterlova B., Cejka J., Zilkova N.: *Microporous Mater.* **1996**, *6*, 405.
9. Cejka J., Zilkova N., Wichterlova B.: *Collect. Czech. Chem. Commun.* **1996**, *61*, 1115.
10. Wood A.: *Chem. Week* **1994**, 17 August, 34.
11. Kaeding W. W., Holland R. E.: *J. Catal.* **1988**, *109*, 212.
12. Bellussi G., Pazzuconi G., Perego C., Girotti G., Terzoni G.: *J. Catal.* **1995**, *157*, 227.
13. Perego C., Amarilli S., Millini R., Bellussi G., Girotti G., Terzoni G.: *Microporous Mater.* **1996**, *6*, 395.
14. Kaeding W. W.: *J. Catal.* **1985**, *85*, 512.
15. Fraenkel D., Levy M.: *J. Catal.* **1989**, *118*, 10.
16. Ivanova I. I., Brunel D., B. Nagy J., Daelen G., Derouane E. G.: *Stud. Surf. Sci. Catal.* **1993**, *78*, 587.
17. Cejka J., Kapustin A. G., Wichterlova B.: *Appl. Catal., A* **1994**, *108*, 87.
18. Ivanova I. I., Brunel D., B. Nagy J., Derouane E. G.: *J. Mol. Catal., A* **1995**, *95*, 243.
19. Cejka J., Zilkova N., Tvaruzkova Z., Wichterlova B.: *Stud. Surf. Sci. Catal.* **1995**, *97*, 401.
20. Reddy K. S. N., Rao B. S., Shiralkar V. P.: *Appl. Catal., A* **1993**, *95*, 53.
21. Beyer H. K., Borbely G.: *Proc. 7th Int. Conf. Zeolites*, p. 867. Kodansha-Elsevier, Tokyo 1987.
22. Zicovich-Wilson C. M., Viruela P., Corma A.: *J. Phys. Chem.* **1995**, *99*, 13224.
23. Blaszkowski S. R., van Santen R. A.: *J. Phys. Chem., B* **1997**, *101*, 2292.
24. Blaszkowski S. R., van Santen R. A.: *J. Am. Chem. Soc.* **1997**, *119*, 5020.
25. Rigby A. M., Kramer G. J., van Santen R. A.: *J. Catal.* **1997**, *170*, 1.
26. Shah R., Gale J. D., Payne M. C.: *J. Phys. Chem., B* **1997**, *101*, 4787.

27. Berthomieu D., Brenner V., Ohanessian G., Denhez J. P., Millie P., Audier H. E.: *J. Am. Chem. Soc.* **1993**, *115*, 2505.
28. Berthomieu D., Brenner V., Ohanessian G., Denhez J. P., Millie P., Audier H. E.: *J. Phys. Chem.* **1995**, *99*, 712.
29. Ratnasamy P., Kumar R.: *Catal. Today* **1991**, *9*, 329.
30. Ernst S.: Personal communication.
31. Dedecek J., Cejka J., Wichterlova B.: *Appl. Catal., B* **1998**, *15*, 233.
32. Hitz S., Prins R.: *J. Catal.* **1997**, *168*, 194.
33. Wichterlova B., Tvaruzkova Z., Sobalik Z.: *Microporous Mesoporous Mater.*, in press.
34. Sponer J. E., Sponer J., Cejka J., Wichterlova B.: *J. Phys. Chem.*, in press.
35. Berthomieu D., Audier H. E., Denhez J. P., Monteiro C., Mourgues P.: *Org. Mass Spectrom.* **1991**, *26*, 271.