

Studies on diisopropylnaphthalene substitutional isomerism

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Abstract

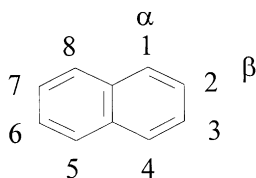
The concentrations of diisopropylnaphthalene (DIPN) isomers in experimental equilibrium mixtures obtained on amorphous aluminosilicate and HY zeolite have been measured by GC method. The total energy and Gibbs free energy of the isomers were calculated by DFT method at the B3PW91/3-21G level. Comparison of the populations based on the DFT energies with the experimental concentrations of DIPN isomers are in good agreement. This fact can suggest that isomerization is mainly determined by thermodynamic equilibrium. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Diisopropylnaphthalene (DIPN); Isomer population; Ab initio; DFT

1. Introduction

Diisopropylnaphthalene (DIPN) mixture is used as a high-quality solvent for copying materials [1]. Especially advantageous in the solvent is high content of 2,7-diisopropylnaphthalene [2]. The 2,6-diisopropylnaphthalene, isolated from the isomeric mixture can be used as a raw material for the production of advanced polyester fibres, films and plastics such as thermotropic liquid crystalline polymers [3].

Theoretically, 10 substitutional isomers are possible, namely: 1,2-, 1,3-, 1,4-, 1,5-, 1,6-, 1,7-, 1,8-, 2,3-, 2,6- and 2,7-diisopropylnaphthalene.



The following isomers of DIPN can usually be detected in the mixture: 1,3-, 1,4-, 1,5-, 1,6-, 1,7-, 2,6- and 2,7- [4–8]. Diisopropylnaphthalene isomers with isopropyl groups placed at adjacent nucleus positions 1 and 2, 1 and 8 or 2 and 3 are frequently not detected in the mixture. However, there are available data in the literature where 2,3-DIPN was detected in the mixture [9,10], or substituents rotation energy in 1,8-DIPN is described [11].

Diisopropylnaphthalene mixtures are prepared mostly from naphthalene or monoisopropylnaphthalene by alkylation or transalkylation reactions. Diisopropylnaphthalene isomers are present in the mixture in different proportions, which depend on the reaction conditions used: catalyst, temperature, contact time, pressure, etc. Generally, diisopropylnaphthalene mixtures obtained under mild reaction conditions and at short contact time are rich in α,α-isomers whereas the ones obtained under more severe conditions and at longer reaction times are enriched in β,β-isomers [6,8]. The α-substitution in the naphthalene nucleus is kinetically more preferred, whereas the β-substitution is thermodynamically more preferred [12].

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However, in the alkylation carried out over shape-selective catalysts, for example mordenite, a high β,β -isomers content in the product is obtained, regardless of temperature and contact time [5,6]. Moreover, higher yield of 2,6- than 2,7-isomer is obtained in diisopropylnaphthalene mixture and, therefore, 2,6-DIPN/2,7-DIPN ratio much higher than 1 is observed. High 2,6-DIPN/2,7-DIPN ratio has been explained by Horsley et al. [13] to be a result of differences in diffusion energy. Recently, Song et al. [14] have calculated with the help of MOPAC programme, frontier electron density values for different positions in the naphthalene nucleus. They have proposed that not only molecule dimensions can play an important role in the shape-selective catalysis but electron densities as well. Position 6 in 2-isopropylnaphthalene has higher electron density than position 7 and, therefore, in the electrophilic substitution in the mordenite channels 2,6-DIPN formation is preferred to 2,7-DIPN.

Entirely different results has been obtained by Moreau et al. [15] who observed that 2,6- and 2,7-disubstituted products were formed in equal yields with a ratio of around 1 when using mordenite and Y-zeolite catalysts for isopropylation with isopropyl bromide and for cyclohexylation with cyclohexyl bromide.

In the reactions conducted over non shape-selective catalysts such as amorphous aluminosilicate equal yields of 2,6-DIPN and 2,7-DIPN were obtained, i.e. 2,6-/2,7- ratio was ca. 1 [8,13]. Moreover, the DIPN mixture obtained in the alkylation of naphthalene with propylene over HL zeolite contained even more 2,7- than 2,6-isomer [5,6,13].

The alkylation is accompanied by many other reactions. Diisopropylnaphthalenes formed in the alkylation take part in such reactions as positional isomerization of alkyl substituent in the naphthalene nucleus, disproportionation, transalkylation, etc.

It is not quite clear to what extent the DIPN isomer distribution in the product reflects the shape-selectivity of the catalyst and to what extent it is overlapped by the isomerization of DIPN or by other side reactions. Even over highly shape-selective catalysts, the 2,6-DIPN/2,7-DIPN ratio decreases with contact time [6,16], probably as a result of approaching thermodynamic equilibrium in the isomerization and other reactions running on external surface of the catalyst.

The knowledge of DIPN distribution in the thermodynamic mixture and theoretical methods to calculate such distribution can be helpful to explain some aspects of shape-selectivity. Therefore, we were obliged to try to establish equilibrium distribution of DIPN isomers at chosen experimental conditions and to indicate possible calculation methods.

2. Experimental

Equilibration reaction, i.e. disproportionation and isomerization of isopropylnaphthalene (IPN) was carried out in a fixed-bed reactor. Amorphous aluminosilicate, HY zeolite and H-mordenite were used as catalysts. The feed (isomeric mixture containing 85.49% of 2-IPN and 14.23% of 1-IPN) was recycled through the catalyst bed with a pump at LHSV of ca. 70 h^{-1} . The reaction was carried out at 250°C for 6 h. Reaction time was long enough to approach equilibrium. Concentration of naphthalene, isopropylnaphthalenes and diisopropylnaphthalenes as well as isomeric distribution of DIPN's remained unchanged for the last several hours of each experiment. For chosen temperature, 6 h was enough to approach thermodynamical equilibrium.

Product samples were analyzed by GC using a 60 m long HP-INNOWAX capillary column and a FID detector. Individual isomers of diisopropylnaphthalene were confirmed by GC/MS, NMR and IR. More detailed description of catalysts and testing procedure is published elsewhere [8].

3. Computational

Each diisopropylnaphthalene molecule can exist in many different conformations due to the flexible isopropyl side chains. Therefore, for each diisopropylnaphthalene molecule, 36 structures (connected to six-fold rotation of each isopropyl group) were optimized at the PM3 semiempirical level by using SPARTAN 5.0.¹ Then, the lowest energy conformer selected from among 36 structures was used as the starting structure for the calculations at the HF/3-21G

¹ Spartan version 4.0.3, Wavefunction, Inc., 18401 Von Karman Ave., #370, Irvine CA 92715.

and B3PW91/3-21G levels by using the Gaussian 94 package [17] running on a SGI computer. Finally, the vibrational spectrum computed analytically and the thermochemical analysis (at $T = 0, 298.15,$ and 523.15 K; $P = 1$ atm) were performed for each of the optimized structures at the B3PW91/3-21G level. No imaginary frequency was found for the B3PW91/3-21G optimized structures. There is a qualitative agreement of the B3PW91/3-21G results with those obtained on HF/3-21G based approach and even the main tendencies can be seen on PM3-based energies. Here, we present the DFT results only as the most reliable out of the three methods.

4. Results and discussion

Isomer populations calculated (Eq. (1)) at the DFT (B3PW91/3-21G) level, based on the total energies (E), zero-point corrected total energies (E_{ZPE} , equal to Gibbs free energies at 0 K), Gibbs free energies at 298.15 K (25°C) (G_{298}) and Gibbs free energies at 523.15 K (250°C) (G_{523}) [18–20] are listed in Table 1.

$$\frac{n_1}{n_2} = \exp\left(\frac{\Delta E}{RT}\right), \quad (1)$$

where n_1/n_2 is isomer population ratio; ΔE the energy difference, $E = E, E_{ZPE}, G_{298}, G_{523}$; RT the thermal factor, and T the temperature fixed to 523.15 K.

The comparison of the isomer population calculated and determined in experimental conditions catalyzed by an amorphous aluminosilicate and HY zeolite at 250°C shows that there is a coincidence between experimental and theoretical tendencies of isomer population. The most abundant (ca. 40% each) are the 2,6- and 2,7-diisopropylnaphthalenes. Next abundant, a matter of a few percent are the 1,3-, 1,6- and 1,7-diisopropylnaphthalenes. The 2,3-isomer is populated about 1% whereas the isomers 1,4- and 1,5- are populated much below 1% but in experimentally detectable amounts. Finally, the experimentally not detected isomers 1,2- and 1,8- are populated in calculations at amounts much below 0.01%.

Some comments to the discrepancies of experimental results obtained over HY zeolite and $\text{Al}_2\text{O}_3\text{-SiO}_2$ catalyst are necessary. The tendencies in isomer populations are similar in both cases, i.e. $2,7 > 2,6 \gg 1,6 > 1,7 \approx 1,3 > 2,3 > 1,4 \approx 1,5$. However, in the case of HY zeolite, the diisopropylnaphthalene mixture is enriched in 2,6- and 2,7-isomers as compared to that obtained over amorphous aluminosilicate, whereas the population of 1,3-DIPN is clearly lowered. Also the content of the rest DIPN isomers is slightly lower in the mixture obtained on HY zeolite than on $\text{Al}_2\text{O}_3\text{-SiO}_2$ catalyst. Two explanations of such results are possible. The first is effect of shape-selectivity on HY zeolite, because 2,6- and 2,7-DIPN are the slimmest of the DIPN isomers. And the second, HY zeolite is known to be a very

Table 1
Distribution of DIPN isomers calculated and determined experimentally at 250°C (mol%)^{a,b}

Isomer	ΔE	ΔE_{ZPE}	ΔG_{298}	ΔG_{523}	Experimental, $\text{Al}_2\text{O}_3\text{-SiO}_2$	Experimental, HY
1,2-DIPN	0.0036	0.0031	0.0024	0.0017	n.d. ^c	n.d.
1,3-DIPN	5.1063	4.8159	3.8794	3.1118	7.90	3.78
1,4-DIPN	0.4708	0.3556	0.1888	0.6580	0.19	0.05
1,5-DIPN	0.4337	0.3198	0.1949	0.7662	0.16	0.08
1,6-DIPN	5.0163	4.6417	3.9052	2.6822	8.49	7.59
1,7-DIPN	2.5109	2.8578	8.8030	12.1517	5.95	4.92
1,8-DIPN	0.0001	0.0001	0.00003	0.0002	n.d.	n.d.
2,3-DIPN	1.4524	1.2644	0.7921	0.4628	0.60	0.40
2,6-DIPN	42.0309	42.5472	41.3530	41.4497	38.04	40.34
2,7-DIPN	42.9750	43.1945	40.8812	38.7158	39.00	42.90

^a Calculations were based on: total energies E at 0 K, zero-point corrected energies E_{ZPE} at 0 K, ΔG_{298} recalculated for 523 K (250°C) and ΔG_{523} .

^b 2,7-DIPN was chosen as comparative isomer. The energies (hartree) for this isomer were as follows: $E = -618.2338337$; $E_{ZPE} = -617.841398$; $G_{298} = -617.955314$; $G_{523} = -617.936292$; 1 hartree = 627.50957 kcal/mol.

^c n.d.: Not detected.

efficient catalyst of transalkylation/disproportionation and isomerization reactions, therefore, isomerization of 1,3-DIPN to 2,6- and 2,7-isomers, which is an intermolecular reaction, runs on HY zeolite more intensively than on amorphous aluminosilicate. This explanation seems to be also reasonable if we consider lowered content of α,α - and α,β -isomers.

The closest agreement between theoretically calculated population and experimentally found for amorphous aluminosilicate or HY zeolite is reached for the total energies or zero-point corrected total energies recalculated for the equilibrium at 250°C. However, the isomers 1,4-, 1,5- and 2,3- seem to be overpopulated and the isomers 1,3-, 1,6- and 1,7- seem to be underpopulated in calculations. For the populations calculated strictly for the free Gibbs energy at experimental condition, i.e. 523.15 K, the 2,6-diisopropyl-naphthalene is the most abundant and the ratio of the 1,6- and 1,7-isomers is reversed. A similar tendency is observed for the populations based on free Gibbs energies at 298.15 K extrapolated to 523.15 K.

Numerous factors may affect the calculated population, based on ΔG_{293} : the frequencies calculated are harmonic not anharmonic and resonances as well as overtones are not included in the thermochemical scheme, the basis set used 3-21G is rather small, the systems are calculated for “vacuum” not for the condensed phase and influence of the intermolecular calculations is neglected, in the real system relaxation from the hot states may be fast while in calculations all the hot states at 523 K are included. However, because we deal with the energy differences some of the perturbations may be cancelled. It happens in calculations that energy differences calculated at lower level of theory fit better to the exact value.

Despite of some disagreements, all the calculated data based on total energies collected in Table 1 strongly suggest thermodynamic equilibrium character of the diisopropyl-naphthalene isomer populations obtained in experiments carried out on amorphous aluminosilicate or HY zeolite.

The comparison of our equilibrium results with experimental results available in the literature confirms that DIPN isomer distribution always runs toward the equilibrium populations determined by us.

Katayama et al. [5] and Sugi and Toba [6] have tested naphthalene alkylation reaction with propylene at 240°C on HY zeolite in a batch type reactor. After

8 h, they have obtained the DIPN mixture with similar isomer distribution. However, their mixture contained higher amount of the 1,3-isomer and lower amount of 2,6 and 2,7 than at equilibrium. From these results we can conclude that the shift of alkyl substituents from position α to position β in the naphthalene nucleus was faster than intermolecular isomerization (i.e. dealkylation/realkylation). Therefore, α,α - and α,β -isomers distributions in the DIPN mixture were very close to the equilibrium, whereas that of 1,3-, 2,6- and 2,7- were not.

Initially high 2,6-DIPN/2,7-DIPN ratio in the alkylation product obtained over H-mordenite catalysts usually lowered with contact time [5,6,16], probably due to the isomerization occurring on the external surface of the catalyst, and slowly became closer to the equilibrium value.

5. Conclusions

The analysis of the DIPN isomers population both theoretically estimated and experimentally detected shows that the most stable and the most abundant isomers are 2,6- and 2,7-DIPN (ca. 40% of each). The contributions of the 1,3-, 1,6-, 1,7- are of the same order (a few percent), whereas ca. 1% of the 2,3-isomer is expected in the mixture. The content of the isomer 1,4- and 1,5- is below 0.5%. The calculations yield the isomer 1,2- and 1,8- to be the most less abundant, whereas in experimental mixture they are not detectable. Our study estimates the concentration level at which the undetected isomers could be expected in experiment.

The calculated data based on total energies suggest thermodynamic equilibrium character of the diisopropyl-naphthalene isomer populations obtained in experiments at amorphous aluminosilicate or HY zeolite.

The results of our calculations can be very helpful to assess shape-selectivity of different catalysts in reactions of diisopropyl-naphthalene mixtures synthesis.

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References

- [1] H.-G. Franck, J.W. Stadelhofer, *Industrial Aromatic Chemistry, Raw Materials Processes Products*, Springer, Berlin, Heidelberg, New York, London, Paris, Tokyo, 1987.
- [2] Y. Okada, M. Akatsu, Y. Ohira, Kureha Chem., European Patent No. 240597, 1990.
- [3] D.E. Stuetz, Celanese Corp., European Patent No. 172012, 1991.
- [4] K. Handrick, *Compendium 76/77 Erdoel Kohle, Erdgas, Petrochem.*, (1976) 308.
- [5] A. Katayama, M. Toba, G. Takeuchi, F. Mizukami, S. Niwa, S. Mitamura, *J. Chem. Soc., Chem. Commun.*, (1991) 39.
- [6] I. Sugi, M. Toba, *Catal. Today* 19 (1994) 187.
- [7] A. Sturaro, G. Parvoli, R. Rella, L. Doretto, *J. Chromatogr. A* 688 (1994) 211.
- [8] R. Brzozowski, W. Tęcza, *Appl. Catal. A* 166 (1998) 21.
- [9] Y. Shiroto, M. Shimura, K. Shimokawa, Y. Fukui, S. Asaoka, H. Tajima, K. Ueda, Y. Tachibana, K. Tate, H. Taniguchi, Chiyoda Corp., NKK, US Patent No. 4950824, 1990.
- [10] Y. Shiroto, M. Shimura, K. Shimokawa, Y. Fukui, Y. Tachibana, K. Tate, H. Taniguchi, Chiyoda Corp., NKK, US Patent No. 4992622, 1990.
- [11] J.E. Anderson, C.J. Cooksey, *J. Chem. Soc., Chem. Commun.* 23 (1975) 942.
- [12] G.A. Olah, J.A. Olah, *J. Am. Chem. Soc.* 98 (1976) 1839.
- [13] J.A. Horsley, J.D. Fellmann, E.G. Derouane, C.M. Freeman, *J. Catal.* 147 (1994) 231.
- [14] C. Song, X. Ma, A.D. Schmitz, H.H. Schobert, *Appl. Catal. A* 182 (1999) 175.
- [15] P. Moreau, A. Finielis, P. Geneste, J. Solofo, *J. Catal.* 136 (1992) 487.
- [16] J.-H. Kim, Y. Sugi, T. Matsuzaki, T. Hanaoka, Y. Kubota, X. Tu, M. Matsumoto, S. Nakata, A. Kato, G. Seo, *C. Pak, Appl. Catal. A* 131 (1995) 15.
- [17] Gaussian 94 (Revision D.4). M.J. Frisch, G.W. Trucks, H.B. Schlegel, P.M.W. Gill, B.G. Johnson, M.A. Robb, J.R. Cheeseman, T.A. Keith, G.A. Petersson, J.A. Montgomery, K. Raghavachari, M.A. Al-Laham, V.G. Zakrzewski, J.V. Ortiz, J.B. Foresman, J. Cioslowski, B.B. Stefanov, A. Nanayakkara, M. Challacombe, C.Y. Peng, P.Y. Ayala, W. Chen, M.W. Wong, J.L. Andres, E.S. Replogle, R. Gomperts, R.L. Martin, D.J. Fox, J.S. Binkley, D.J. Defrees, J. Baker, J.P. Stewart, M. Head-Gordon, C. Gonzales, J.A. Pople, Gaussian, Inc., Pittsburgh, PA, USA, 1995.
- [18] J.W. Ochterski, *Thermochemistry in Gaussian*, help@gaussian.com, © 2000, Gaussian Inc.
- [19] J.B. Foresman, E. Frish, *Exploring Chemistry with Electronic Structure Methods: A Guide to Using Gaussian*, 2nd Edition, Pittsburgh, PA, USA, 1996.
- [20] P. Garnuszek, J.Cz. Dobrowolski, A.P. Mazurek, *J. Mol. Struct. (Theochem.)* 507 (2000) 145.