

The modelling *via* methods of molecular dynamics of influence of zeolites with $(\text{Na}^+_x(\text{H}_2\text{O})_y)[\text{Al}_a\text{Si}_b\text{O}_c]$, $\text{Ca}_x[\text{H}_2\text{O}]_y\text{Al}_a\text{Si}_b\text{O}_c$, Si_xO_y frame work types on formation hydrogenated pyrans by Prins reaction

© Pavel A. Pasko,⁺ Ivan V. Vakulin,^{*} and Rifkat F. Talipov
Bashkir State University. Zaki Validi St., 32. Ufa, 450076. Russia.
Phone/fax: +7 (347) 229-97-29. E-mail: pasko.pav62@gmail.com

^{*}Supervising author; ⁺Corresponding author

Keywords: Prins reaction, hydrogenated pyrans, molecular dynamics, transition state, zeolites.

Abstract

The possibility of selective stabilization of the transition state of the formation of 4-alkyl-substituted hydrogenated pyrans by the Prins reaction in the presence of zeolites of the elemental composition $\text{Na}^+_x(\text{H}_2\text{O})_y[\text{Al}_a\text{Si}_b\text{O}_c]$, $\text{Ca}_x[\text{H}_2\text{O}]_y\text{Al}_a\text{Si}_b\text{O}_c$, $\text{Al}_a\text{P}_b\text{O}_c$ is demonstrated by molecular dynamics methods using the Universal forcefield. As model alkenes, ethylene, propylene, isobutylene, butene-1 and butene-2 were used. The formation of hydrogenated pyrans by the Prins reaction is considered as the addition of a formaldehyde dimer over a multiple bond of the alkene. The participation of formaldehyde dimers in the formation of 1,3-dioxanes and hydrogenated pyrans by the Prins reaction, as well as the ratio of the thermodynamic parameters of these processes are justified by our previous studies. Structures of transition states are found in the approximation MP2/6-31G(d,p) and correspond to the addition reaction of the dimer of formaldehyde by the multiple bond of the alkene. The energy of the interaction of transition states with the cavities of zeolites was estimated using "frozen" structures. The nature of the interaction and the energy of stabilization of transition states on materials with a developed surface were determined using the Adsorption Locator module in the software package Accelrys Material Studio 5.5.

It is shown that the energy of stabilization of the transition states depends on pore diameter of the zeolites, and the dependence found is of an extreme character. The maximum stabilization is achieved with pore sizes of zeolites comparable to the linear sizes of the transition state, in which case it is placed in the cavity. It has been established that the elemental composition of zeolites does not significantly affect the magnitude of the stabilization effect and the pore diameter at which it is observed. According to the calculations, the pore diameter of the zeolites of the groups examined, at which the maximum stabilization of the transition state is observed, is in the range 6.0-7.5 Å.

References

- [1] I.V. Vakulin, O.Yu. Kupova, R.F. Talipov. *Bulletin of Bashkir University*. **2011**. Vol.16. No.3. P.694-697. (russian)
- [2] O.Y. Kupova, I.V. Vakulin, R.F. Talipov. Ab initio study of 1,3-dioxanes formation from formaldehyde dimer and alkenes. *Computational and Theoretical Chemistry*. **2013**. P.57-61.
- [3] O.Y. Kupova, I.V. Vakulin, R.F. Talipov, G.R. Talipova, N.D. Morozkin. Theoretical investigation of the role of formaldehyde dimers in the Prins reaction. *Reaction kinetics, mechanisms and catalysis*. **2013**. Vol.110. No.1. P.41-52.
- [4] R.R. Syrlybaeva, I.V. Vakulin, R.F. Talipov. *Vestnik Bashkirskogo universiteta*. **2007**. Vol.12. No.3. P.20-22. (russian)
- [5] O.Yu. Kupova, I.V. Vakulin, G.R. Talipova, and R.F. Talipov. Quantum chemical research of 1,3-dioxanes formation from formaldehyde dimer and alkenes. *Butlerov Communications*. **2012**. Vol.32. No.13. P.123-127. ROI: jbc-02/12-32-13-123
- [6] A.A. Granovsky. <http://classic.chem.msu/gran/gamess/index.html>
- [7] K. Morihara, S. Kawasaki, M. Kofuji, T. Shimada. Footprint Catalysis. VI. Chiral “Molecular Footprint” Catalytic Cavities Imprinted by a Chiral Template, Bis(*N*-benzyloxycarbonyl-L-alanyl)amine, and Their Stereoselective Catalyses. *Bull. Chem. Soc. Jpn.* **1993**. Vol.66. P.906-913.

- [8] K. Morihara, S. Doi, M. Takiguchi, T. Shimada. Footprint Catalysis VII. Reinvestigation of the Imprinting Procedures for Molecular Footprint Catalytic Cavities: The Effects of Imprinting Procedure Temperature on the Catalytic Characteristics. *Bull. Chem. Soc. Jpn.* **1993**. Vol.66. P.2977-2982.
- [9] K. Morihara, T. Iijima, H. Usui, T. Shimada. Footprint Catalysis. VIII. Molecular Imprinting for Footprint Cavities on an Active Clay Surface. *Bull. Chem. Soc. Jpn.* **1993**. Vol.66. P.3047-3052.
- [10] T. Shimada, R. Hirose, K. Morihara. Footprint Catalysis. X. Surface Modification of Molecular Footprint Catalysts and Its Effects on Their Molecular Recognition and Catalysis. *Bull. Chem. Soc. Jpn.* **1994**. Vol.67. P.227-235.
- [11] K. Morihara, M. Takiguchi, T. Shimada. Footprint Catalysis. XI. Molecular Footprint Cavities Imprinted with Chiral Amines and Their Chiral Molecular Recognition. *Bull. Chem. Soc. Jpn.* **1994**. Vol.67. P.1078-1084.
- [12] T. Matsuishi, T. Shimada, K. Morihara. Footprint Catalysis. IX. Molecular Footprint Catalytic Cavities Imprinted with Chiral Hydantoins; Enantioselective Hydantoinase Mimics. *Bull. Chem. Soc. Jpn.* **1994**. Vol.67. P.748-756.
- [13] C. Gonzalez, H.B. Schlegel. An Improved Algorithm for Reaction-Path Following. *J. Chem. Phys.* **1989**. Vol.90. No.4. P.2154-2161.
- [14] C. Gonzalez, H.B. Schlegel. Reaction-Path Following in Mass-Weighted Internal Coordinates. *J. Phys. Chem.* **1990**. Vol.94. No.14. P.5523-5527.
- [15] T. Matsuishi, T. Shimada, K. Morihara. Definitive Evidence for Enantioselective Catalysis over "Molecular Footprint" Catalytic Cavities Chirally Imprinted on a Silica(Alumina) Gel Surface. *Chem. Lett.* **1992**. Vol.21. No.10. P.1921-1924.
- [16] T. Shimada, R. Kurazono, K. Morihara. Footprint Catalysis. V. Substituent Effects of Template Molecules on the Catalytic Behavior of Imprinted Molecular Footprint Cavities. *Bull. Chem. Soc. Jpn.* **1993**. Vol.66. P.836-840.
- [17] I.V. Vakulin, O.Yu. Kupova, G.R. Talipova, E.R. Latypova, R.F. Talipov. *Bulletin of Bashkir University.* **2014**. Vol.19. No.4. P.1164-1167. (russian)