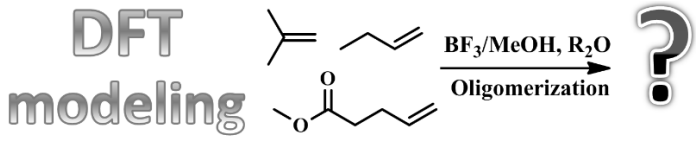
DFT MODELING AND VISUALIZATION OF THE MECHANISMS OF BF_3/ROH-CATALYZED CATIONIC OLIGOMERIZATION OF OLEFINS

Ivchenko P.V.[(1,2)], *Pyatakov D.A.*[(1)], *Tavtorkin A.N.*[(1)], *Nifant'ev I.E.*[(1,2)]
[(1)] A.V. Topchiev Institute of Petrochemical Synthesis RAS
119991, Moscow, Leninsky pr. 29
[(2)] M.V. Lomonosov Moscow State University
119991, Moscow, Leninskie Gory 1–3

Oligomerizations of 2-methylprop-1-ene (isobutylene, IB) and dec-1-ene (DE) occupy a special place among industrially implemented processes, both are based on the use of BF_3/ROH catalyst, but result in the formation of different products – highly reactive polyisobutylenes with DP_n ~ 10–50, and dec-1-ene oligomers with a high trimer content. Despite the practical importance of these processes, their mechanistic studies are fragmentary and at times contradictory. Recently, oligomerization of polar vinyl monomers of the formula $X(CH_2)_nCH=CH_2$ (X = –CH_2OH, –COOR, –COOH; n = 7, 8), which are the products of modern oleochemistry, has also caught the attention of researchers. The primary goal of our study was the comparison of IB, linear α-olefin, and polar vinyl monomer in BF_3/ROH catalyzed oligomerization.

DFT modeling of the IB polymerization initiated by $[GaAr_2]^+$, $(AlCl_3)_2H_2O$, sulfated polymers and other species is presented in the literature, but BF_3/ROH catalyzed reaction remaines unexplored to date from the theoretical point of view. The analysis of the mechanism of DE oligomerization usually focuses on the simplest cationic model, and specific role of the BF_3/ROH catalytic system has also remained offscreen.



Based on experimental results, we have analyzed the mechanisms of BF_3/ROH catalyzed oligomerization of IB, DE and methyl undec-10-enoate using DFT modeling. The newly developed concept implies the participance of two olefin molecules and $(BF_3{\cdot}ROH)_2$ as an initiator, the role of the ether additives is to provide high *exo*-selectivity of isobutylene oligomerization. This concept argues the chain-growth oligomerization with intermediate retention of the cationic center (IB), or H^+ elimination (linear α-olefins) explaining the preferable formation of trimers.

In this way, DFT modeling allowed to explain some key experimental features of the olefin cationic oligomerization, and the results of mechanistic simulations can be used in further development of the cationic catalysts of this industrially significant process.

This work was supported by Russian Science Foundation (Grant No. 24-43-20016).