Olefin epoxidation by molybdenum peroxo compound : molecular mechanism characterized by the electron localization function and catastrophe theory.

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Streszczenie

The oxygen atom transfer reaction from the Mimoun-type complex $MoO(\eta^2\text{-}O_2)_2OPH_3$ to ethylene C_2H_4 affording oxirane C_2H_4O has been investigated within the framework of the Bonding Evolution Theory in which the corresponding molecular mechanism is characterized by the topological analysis of the electron localization function (ELF) and Thom's catastrophe theory (CT). Topological analysis of ELF and electron density analysis reveals that all Mo−O bonds in $MoO(\eta^2\text{-}O_2)_2OPH_3$ and $MoO_2(\eta^2\text{-}O_2)OPH_3$ belong to closed-shell type interactions though negative values of total energy densities $E^e(\mathbf{r}_{BCP})$ imply some covalent contribution. The peroxo O_i—O_j bonds are characterized as charge-shift or protocovalent species in which pairs of monosynaptic basins $V_3(O_i)$, $V_3(O_j)$ with a small electron population of ∼0.25e each, are localized between core basins $C(O_i)$, $C(O_j)$. The oxygen transfer reaction from molybdenum diperoxo complex $MoO(\eta^2\text{-}O_2)_2OPH_3$ to C_2H_4 system can be described by the following consecutive chemical events: (a) protocovalent peroxo O_2−O_1 bond breaking, (b) reduction of the double C_1═C_2 bond to single C_1−C_2 bond in ethylene, (c) displacement of oxygen O_1 with two nonbonding basins, $V_{i=1,2}(O_1)$, (d) increase of a number of the nonbonding basins to three ($V_{i=1,2,4}(O_1)$); (e) reorganization and reduction in the number of nonbonding basis to two basins ($V_{i=1,4}(O_1)$) resembling the ELF-topology of the nonbonding electron density in oxirane, (e) formation of the first O_1−C_2 bond in oxirane, (f) C_2−O_1—C_2 ring closure, (g) formation of singular nonbonding basin $V(O_2)$ in new Mo═O_2 bond. The oxygen atom is transferred as an anionic moiety carrying a rather small electronic charge ranging from 0.5 to 0.7e.