Catalytic Effects on Kinetics of the Stone-Wales Isomerizations: Computations of the N and CN Cases

Zdenvek Slanina,[1] Filip Uhlik,[2] Shyi-Long Lee[3] and Ludwik Adamowicz[4]

[1]Institute of Chemistry
Academia Sinica, 128 Yen-Chiu-Yuan Rd., Sec.2
Nankang
Taipei, ROC 11529
Taiwan - R. O. C.

[2]Charles University
Department of Physical and Macromolecular Chemistry,
School of Science
Albertov 6
Prague 2, CZ 12843
Czech Republic

[3]National Chung-Cheng University
Department of Chemistry, Ming-Hsiung
Chia-Yi, ROC 621
Taiwan - R. O. C.

[4]University of Arizona
Department of Chemistry, 1306 E. University Blvd.
Tucson, AZ 85721-0041
U. S. A.

The Stone-Wales transformation (A. J. Stone and D. J. Wales, Chem. Phys. Lett. **128** (1986) 501) represents an important concept of fullerene science. It has been a rather hypothetical cage isomerization process for rearrangements of the rings in fullerenes and nanotubes. It can be viewed as a movement of two carbon atoms during which two bonds are broken and thus, it is not necessarily a convenient, feasible kinetic process. In fact, it is thermally (but not photochemically) forbidden. In the past, we tried to reduce the isomerization activation barriers through kinetics in an electronically excited state. However, we have recently focused on the kinetic barriers for the Stone-Wales rearrangement influenced by catalytic actions by means of free atoms or small clusters. The catalytic effects on the kinetics of the Stone-Wales fullerene transformation are computed here in a more detailed way for two catalytic agents: N atoms and CN radicals. The CN group is considered also because KCN catalysis has in fact been used for (supposed) opening of the fullerene cage (R. J. Cross and M. Saunders, PV 2001-11, ECS, Pennington, 2001, p. 298). The computations are performed at semiempirical and DFT levels on a model bowl-shaped fragment $C_{34}H_{12}$. The *ab initio* density-functional computations have however been performed in the fixed, mostly PM3 optimized geometries, i.e., B3LYP/6-31G*//PM3.