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Computational modeling of the elemental catalysis in the Stone–Wales fullerene rearrangements

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Abstract

Catalytic effects on the kinetics of the Stone–Wales fullerene transformation are studied computationally. The catalytic agents are represented by free elements, neutral or charged. The computations are performed at semiempirical (PM3) and DFT (B3LYP/6-31G*//PM3) levels on a model bowl-shaped fragment $C_{34}H_{12}$. The semiempirical and DFT activation energies agree reasonably well. In all computed cases, the activation barrier is lowered compared with that of the uncatalyzed reaction. The kinetic barriers for the catalyzed rearrangements increase in the following order: N, H, O, P, S, B, Cl, C, F, Li, Se, Fe, Hg, Zn, Si, Sn, Ge, Mg, and Al. Nitrogen atoms are pointed out as especially potent catalytic agents. At the PM3 computational level, the isomerization kinetic barrier is reduced to 193, 110, and 342 kJ mol^{-1} for the N^+, N, and N^- species, respectively. If the activation barriers are re-computed at the B3LYP/6-31G*//PM3 level, they are changed to 76, 105, and 323 kJ mol^{-1} for the N^+, N, and N^- species, respectively. As small amounts of nitrogen (as well as other elements) are available in virtually any kind of fullerene synthesis, the study offers a computational support for kinetic feasibility of the Stone–Wales fullerene transformation.

Keywords: Fullerene; Molecular orbital calculations; Rearrangements; Catalysis

1. Introduction

At a very early stage of fullerene science, Stone and Wales suggested [1] a formal isomerization process that provides a general hypothetical mechanism for interconversions between fullerene isomers [2,3]. The pyracylene rearrangement has commonly been called the Stone–Wales transformation. The Stone–Wales transformation represents a useful concept of fullerene science, important for topological and mechanistic reasoning. However, it has represented a somewhat hypothetical cage isomerization process for rearrangements of the rings in fullerenes as its direct observation has not been reported yet. It can be viewed (Fig. 1) 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 [2] forbidden according to the Woodward–Hoffman rules for concerted reactions [4].

The Stone–Wales rearrangement has frequently been computed [5]. Stanton [6] computed the reaction energetics at the MNDO level. Scuseria and co-workers examined [7] kinetics of the Stone–Wales transformation as an essential part of fullerene annealing and fragmentation. They conclude that a non-concerted process with an sp^3 intermediate (Fig. 1) should be more convenient than an in-plane concerted mechanism. This finding is also in agreement with the fact that the non-concerted process is not Woodward–Hoffman forbidden. This sp^3 non-concerted mechanism has further been computed [8–11]. The Stone–Wales transformation can produce comprehensive topological maps for interconversions of fullerene isomers [12]. The transformation can also be generalized [13]. Walsh and Wales [14] recently treated the C_{60} isomerizations as a complex kinetic scheme, using the master equation

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approach [15] and a density-functional tight-binding potential. Their approach offers an explanation for the relatively long C_{60} relaxation times.

Even if the sp^3 non-concerted mechanism for the Stone–Wales rearrangement is considered, the computed [7] activation barriers remain relatively high. It has been known that kinetic barriers in fullerene reactions can be reduced [16] through photochemical mechanisms. Indeed, we tried to reduce [9] the isomerization activation barriers through kinetics in an electronically excited state (triplet state). However, it has turned out [9–11] that the barrier lowering through photochemical mechanism is not really significant for the Stone–Wales transformation. Recently, another way how to obtain a kinetically feasible Stone–Wales rearrangement has been considered, namely catalysis by means of free atoms or small atomic clusters. In particular, an autocatalysis by free carbon atoms has been considered by Eggen et al. [17,18]. Their catalytic complex has stoichiometry C_{61}, also treated in previous experiments and computations [19–21]. However, the autocatalytic computations were performed with a local spin density functional. It has been known [22,23] that some density-functional techniques can have a poor performance for carbon clusters.

We have been interested [24–26] in isomeric fullerenes and their equilibrium isomeric mixtures. The inter-isomeric equilibrium should be established, inter alia, by means of the Stone–Wales rearrangements, both simple and generalized. Therefore, we have constantly been interested in relatively fast kinetic processes that can really efficiently establish the inter-isomeric equilibrium. Graphite always contains small amounts of various chemical elements [27]. Similarly, N_2 and O_2 also come as an impurity in the inert gas used as the medium for the fullerene synthesis. Moreover, some metals may originate from the electrical wires in the graphite-arc apparatus. Hence, one can expect presence of small, and sometimes even substantial amounts of non-carbon atoms in the reaction mixture, both in graphite-arc and combustion fullerene synthesis. In this article, we report model computations of a series of potential candidates, both metals and non-metals, acting in the catalyzed Stone–Wales transformation.

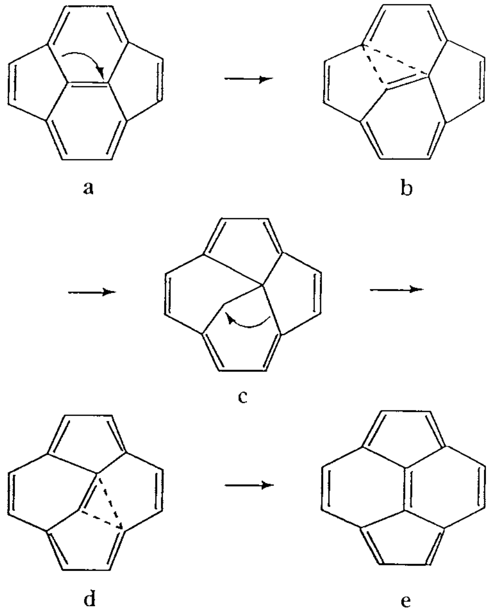

Fig. 1. Scheme of the non-concerted mechanism for the Stone–Wales rearrangement of reactant (a) to product (e) through an intermediate (c); the rearrangement is mediated by two activated complexes (b) and (d).

2. Computations

The computations have been performed using both semiempirical and nonempirical quantum-chemical methods. The semiempirical treatment is based on three methods [28–30]: AM1, PM3, and SAM1. However, the PM3 approach is prevailing and other two methods are only applied if the PM3 parameterization is not available. The computations were carried out with the MOPAC [31], SPARTAN [32], and AMPAC [33] program packages. The calculations started with geometry optimization at semiempirical level for both reactant and related activated complex. The geometry optimizations were performed with no symmetry constraints in Cartesian coordinates, and with analytically constructed energy gradient. Once a stationary point was reached, the harmonic vibrational analysis was carried out by a numerical differentiation of the analytical energy gradient. The vibrational analysis checked nature of the located stationary point through the number of imaginary vibrational modes. Moreover, the vibrational eigenvector belonging to the imaginary frequency in the case of an activated complex was analyzed in order to assign the related reactant/product. In some cases the assignment was further checked by means of reaction-path calculations. The computations were performed for singlet electronic state. Hence, in order to avoid an open shell configuration, some atoms had to be treated as cations or anions. In one case, namely nitrogen atom, open shell configuration was allowed and treated through unrestricted Hartree–Fock approach [34] (UHF).

For selected cases, the inter-isomeric energetics was further evaluated at ab initio density-functional level, mostly with the B3LYP/6-31G* approach implemented in the G94 and G98 program packages [35,36]. The ab initio density-functional computations were however performed in the fixed, mostly PM3 optimized geometries, i.e. B3LYP/6-31G*//PM3. In a few cases, other basis sets had to be used owing to either computational demands or convergency difficulties. Then, the standard 3-21G [34] or CEP-31G [37–39] basis sets were applied (Table 1).

Table 1
Simulation of the catalyzed Stone–Wales transformation at $C_{34}H_{12}$ fragment

System [a]	$\Delta E_1^{\neq}$ (kJ mol^{-1})	
	PM3	B3LYP/6-31G*
$C_{34}H_{12}$	509	519
N and $C_{34}H_{12}$	110	105
N^+ and $C_{34}H_{12}$	193	76
N^- and $C_{34}H_{12}$	342	323
H^- and $C_{34}H_{12}$	152	
O and $C_{34}H_{12}$	244	265
P and $C_{34}H_{12}$	324	
S and $C_{34}H_{12}$	368	
B^+ and $C_{34}H_{12}$	377 [b]	358
Cl^- and $C_{34}H_{12}$	379	
C and $C_{34}H_{12}$	386	333
F^- and $C_{34}H_{12}$	397	
Li^+ and $C_{34}H_{12}$	408	439
Se and $C_{34}H_{12}$	418	
Fe and $C_{34}H_{12}$	437 [c]	376 [d]
		357 [e]
Hg and $C_{34}H_{12}$	439	
Zn and $C_{34}H_{12}$	442	
Si and $C_{34}H_{12}$	447	
Sn and $C_{34}H_{12}$	449	
Ge and $C_{34}H_{12}$	460	
Mg and $C_{34}H_{12}$	490	369
Al^+ and $C_{34}H_{12}$	541	425

[a] Catalysis by various adsorbed elements X: X and $C_{34}H_{12}$.
[b] AM1.
[c] SAM1.
[d] B3LYP/3-21G.
[e] B3LYP/CEP-31G.

3. Results and discussion

The reported computations have been performed on a fragment of a bowl-like shape already employed in our previous studies [8–11]. We have preferred this model fragment over the complete C_{60} sphere purely owing to computational economy. The fragment has stoichiometry $C_{34}H_{12}$ and its PM3 optimized structure is presented in Fig. 2. As already mentioned, we are interested here in the sp^3 non-concerted mechanism. Hence, we proceed from the reactant (local minimum) to the first activated complex, then an intermediate (another local minimum) follows, and through the second activated complex the product is reached (local minimum). Owing to the symmetry of our model fragment, we in fact deal with an autoisomerization or degenerate rearrangement (Fig. 1). We are primarily interested in the activation energy from the reactant to the first activated complex, $\Delta E_1^{\neq}$. Without any catalysis, the activation energy is almost identical in the PM3 and B3LYP/631G*//PM3 approaches, being 509 and 519 kJ mol^{-1}, respectively (Table 1).

In order to have some standard for comparison, we have tried to suggest some reasonable value for $\Delta E_1^{\neq}$, such that the Stone–Wales rearrangement will be a kinetically feasible process. For that purpose we can select an arbitrary half-life of 1 s for a general unimolecular process. Of course, it is a rather arbitrary value and some smaller term could be considered as well. In addition, we do not know what a reasonable half-time should be, and we also do not know what is actually a typical temperature in fullerene synthesis. If we for example consider temperatures of 800, 1000, and 1500 K, the selected half-life of 1 s requires the activation energy of 205, 258, and 392 kJ mol^{-1}. If we now combine this simple reasoning with the lowest activation barrier found by Eggen et al. [17], we could place a reasonable value for the $\Delta E_1^{\neq}$ term somewhere around 250 kJ mol^{-1}. It is interesting to note that the master equation approach of Walsh and Wales [14] would require temperatures of 1900–2300 K to get expected predictions (in fact, their density-functional tight-binding potential barrier may be underestimated).

Let us move now to the catalyzed Stone–Wales transformation. Hence, we select various atoms, primarily limiting our considerations to those atoms that are parameterized in the program implementation of at least one of the three semiempirical methods considered (PM3, AM1, SAM1). The selected atom is placed above the model half-sphere in the vicinity of the critical bond and the structure is completely optimized (Fig. 3). Later on, a reasonable starting structure for

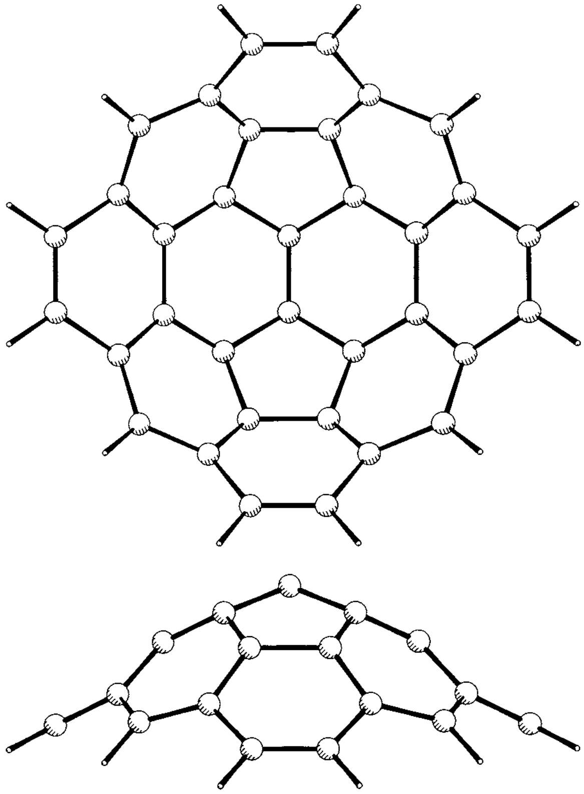

Fig. 2. Two views of the PM3 optimized structure of the $C_{34}H_{12}$ fragment.

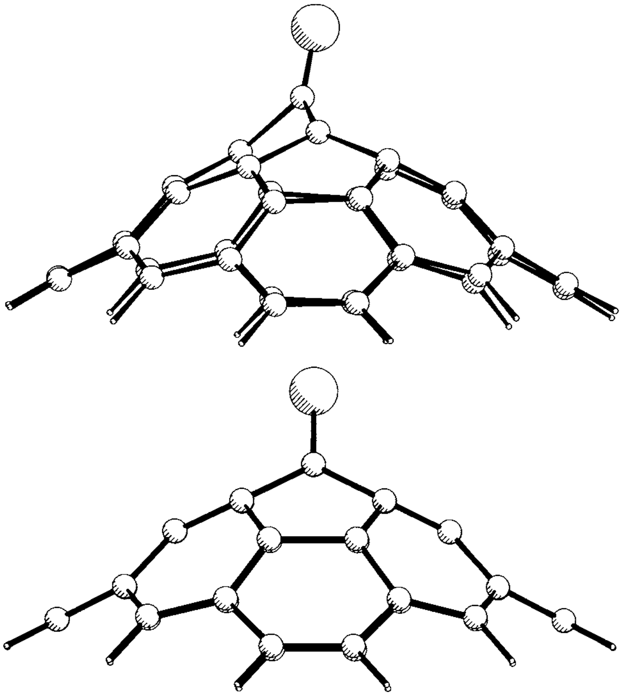

Fig. 3. The PM3 optimized structures of the reactant (bottom) and transition state (top) in the system O and $C_{34}H_{12}$.

the related activated complex is created and optimized within a transition-state option. Fig. 3 illustrates the results on the O and $C_{34}H_{12}$ system. In fact, the reactant actually exhibits the well-known 6/6 structure [40–43]. This 6/6 epoxide-like structure is the only $C_{60}O$ isomer known from experiment [41] (its preferential formation seems to be kinetically controlled [43]). Moreover, the critical 6/6 bond is symmetrically placed in the center of our model (while the 5/6 bonds are already side-shifted in our model and thus more perturbed). As in the majority of other cases, also for the O and $C_{34}H_{12}$ system the PM3 and B3LYP/6-31G*// PM3 treatments give well comparable $\Delta E_1^{\neq}$ values of 244 and 265 kJ mol^{-1}, respectively. The following atoms (or their ions) have been considered (already organized according to the semiempirical activation energies, Table 1): N, H, O, P, S, B, Cl, C, F, Li, Se, Fe, Hg, Zn, Si, Sn, Ge, Mg, and A1.

The key finding from the data of Table 1 is that in all the computed catalytic models the activation energy is lower than in the non-catalyzed situation. This is true for the results from both methods, if available, with an exception of Al^+. In four cases the computed value is lower than our threshold of 250 kJ mol^{-1}. Interestingly enough, simple non-metals offer a better choice over the metals considered. In particular, nitrogen atoms exhibit significant catalytic properties. At the PM3 level the $\Delta E_1^{\neq}$ potential barrier is reduced to 193, 110, and 342 kJ mol^{-1} for the N^+, N, and N^- species, respectively. If the activation barriers are recomputed at the B3LYP/631G*//PM3 level, they are changed to 76, 105, and 323 kJ mol^{-1} for the N^+, N, and N^- species, respectively. Although the semiempirical and density-functional terms somewhat differ, they mostly reach significantly low values.

We have also been evaluating simple metal oxides as potential catalytic agents and our preliminary results are encouraging. In fact, metal oxides can be more potent catalysts than pure metal atoms. For example, while the B3LYP/6-31G*//PM3 value for Al^+ is 425 kJ mol^{-1}, it drops to 249 kJ mol^{-1} for AlO_2^+. It will of course depend on particular reaction conditions if the catalytic agents will have a form of oxides, small atomic clusters or single free atoms. While in the electric-arc fullerene synthesis decomposition to single atoms is more likely, production of fullerenes by combustion and in geological materials [25] should allow also for presence of oxides in the hot reaction mixture.

4. Concluding remarks

This paper points out the interesting possibility that various atoms, both metals and non-metals, can efficiently lower the kinetic barrier in the Stone–Wales rearrangements. At this early stage we cannot answer the question what is the best catalyst for the rearrangements. More effort is needed to expand the set of the treated atoms and to check the theoretical tools applied. In some cases, larger basis sets should be employed as well as the ROHF treatment, and even relativistic effects should be estimated. Moreover, one should side by side compute closed- and open-shell systems [44]. While in this paper we concentrated on the central stage of the catalyzed Stone–Wales transformation, we should also later on describe its initial phase (creation of the substrate–catalyst complex) and its terminal phase (release of the free substrate after the isomerization). The computations should help in both optimization of fullerene production methods and explanation of naturally occurring fullerenes supposedly formed under relatively mild conditions [45].

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