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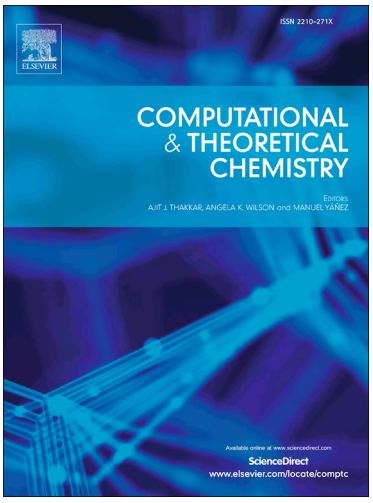

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PII: S2210-271X(18)30101-4
DOI: https://doi.org/10.1016/j.comptc.2018.03.019
Reference: COMPTC 2753

To appear in: *Computational & Theoretical Chemistry*

Received Date: 26 January 2018
Revised Date: 7 March 2018
Accepted Date: 19 March 2018

Please cite this article as: A. Nouri, E. Zahedi, M. Ehsani, A. Nouri, E. Balali, Understanding the kinetics and molecular mechanism of the Curtius rearrangement of 3-oxocyclobutane-1-carbonyl azide, *Computational & Theoretical Chemistry* (2018), doi: https://doi.org/10.1016/j.comptc.2018.03.019

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Understanding the kinetics and molecular mechanism of the Curtius rearrangement of 3-oxocyclobutane-1-carbonyl azide

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ABSTRACT

The approach presented here is an unprecedented insight into the understanding of kinetics and molecular mechanism of thermal Curtius rearrangement of 3-oxocyclobutane-1-carbonyl azide. Curtius rearrangement can proceed via concerted and stepwise mechanisms. The CBS-QB3 and CBS-APNO composite methods indicated that concerted pathway is dominant and 10^4-10^5 times faster than stepwise path. The bonding evolution theory analysis at the B3LYP/6-311G(*d*,*p*) revealed that the reaction via concerted pathway can be described with catastrophe sequence 9-$CF^{\dagger}C^{\dagger}{}^{\mathbf{TS}}FC^{\dagger}FC^{\dagger}C$-0 by the following chemical events: (a) change of topological signature of N_2–N_3 bond; (b) increasing the number of non-bonding monosynaptic attractor on N_1 atom; (c) breaking of N_1–N_2 bond and extrusion of nitrogen molecule; (d) decreasing the number of non-bonding monosynaptic attractors on N_1 atom; (e) breaking of C_4–C_5 bond and formation of *pseudoradical* centers on the C_4 and C_5 atoms; (f) annihilation of *pseudoradical* center on the C_5 atom; (g) change of topological signature of N_1–C_5 bond; and (h) formation of N_1–C_4 bond. Along the reaction course electron flow redistribution is asynchronous and bond breaking/forming do not takes place simultaneously demonstrating that the reaction is concerted yet highly asynchronous process.

Keywords: Curtius rearrangement; molecular mechanism; ELF; catastrophe theory; BET

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