

Application of the Cplex-isoelectronic theory to electrocyclisations, sigmatropic rearrangements, cheletropic reactions and antiaromaticity Consistent with Santilli's hadronic chemistry

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Abstract

The recently proposed Cplex-isoelectronic theory is applied to electrocyclisation/ring opening reactions, sigmatropic rearrangements, cheletropic reactions and antiaromaticity. The Cplex-isoelectronic theory is consistent with the experimental data and makes different predictions from the present quantum chemical methods in some cases, namely a stepwise pathway for the conrotatory photochemical ring opening of 1,3-cyclohexadiene, a concerted photochemical electrocyclisation for 1,3-cyclohexadiene via disrotatory motion, a concerted suprafacial [1,5] sigmatropic shift with inversion for norcaradiene, a concerted suprafacial [1,3] carbon shift with inversion and retention, a concerted suprafacial photochemical [1,5] hydrogen migration, a concerted photochemical [3,3] shift, stabilisation of cyclic $4n\pi$ electron systems by delocalisation and their excess energy is due only to electronic repulsion and strain, the monohomocyclopropenium and cyclopropenyl cations are not 'aromatic'. The available empirical evidence is consistent with these new predictions. This finding is consistent with Santilli's hadronic chemistry which proposes that the present quantum chemical theories require the addition of a small correction factor for molecules with two or more electrons. It is also consistent with the fact that it is impractical to calculate an exact representation for complex chemical systems using quantum based methods. Replacing double bonds with strained systems, such as the norbornene ring, is predicted to convert stepwise pathways to concerted. © 2007 International Association for Hydrogen Energy. Published by Elsevier Ltd. All rights reserved.

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1. Introduction

Recently a new theory of pericyclic chemistry and aromaticity was proposed, the Cplex-isoelectronic theory [1]. This new qualitative theory is based on the chemical level of the reductional hierarchy, in line with the old electronic theory of

Robinson and Ingold, and is not based on quantum mechanics. It makes logical and scientific connections and regularities between known and unknown systems, an approach seen in the emerging area of Complexity theory. The Cplex-isoelectronic theory is consistent with the empirical data. It also makes predictions that are different from the present quantum chemical methods [2] and the experimental evidence, when available, is found to be consistent with this new chemical theory [1]. Nobel prizes have been awarded for the quantum chemical methods. It is conceivable that the present quantum based methods can make inaccurate predictions for *complex* systems due to indeterminacy, assumptions, diversity of factors involved, intractable calculations and chaos [1]. Furthermore Santilli's hadronic mechanics claims that quantum mechanics requires a correction, due to the deep overlap of the wavepackets of the valence electrons at short distance, for molecules with two or

Abbreviations: ADEP, antiperiplanar dynamics of isoelectron pairs; AFS, acceptor at the final facial selectivity site; ASIED, acceptor site of initial electron dynamics; CWP-SDSE, continuous when planar-SDSE; DFS, donor at the final facial selectivity site; DSIED, donor site of initial electron dynamics; FSED, final facial selectivity of electron density; RCEDGD, rate of continuous electron dynamics greater than delocalisation; SEADEF, substituent electronic assistance in the direction of the electron flow; SDSE, synperiplanar dynamics of single isoelectrons; SDEP, synperiplanar dynamics of isoelectron pairs

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more electrons [3]. Expansion of the Cplex-iso-electronic theory into the hadronic and quantum level is for the future once this new theory is fully developed on the chemical level.

The Cplex-iso-electronic theory assumes that isoelectron pairs move in an antiperiplanar manner (ADEP) while single isoelectrons move in a synperiplanar manner (SDSE) [1]. The ADEP process is favoured over the SDSE in most thermal reactions whereas the SDSE is favoured under photochemical conditions. Only in strained systems is synperiplanar dynamics of isoelectron pairs (SDEP) more efficient than the ADEP. These assumptions are deduced from nucleophilic, radical addition, S_N2 and S_N2' reactions and the anomeric effect. There is direct evidence for these dynamics in pericyclic reactions and in aromatic compounds [1].

The objective of this paper is to outline the Cplex-iso-electronic theory for electrocyclisation/ring opening reactions, sigmatropic rearrangements, cheletropic reactions and antiaromaticity. Again this new theory makes different predictions from the present quantum chemical methods and the available empirical evidence is consistent with the Cplex-iso-electronic theory. This finding is thus consistent with Santilli's hadronic chemistry [3]. Exploring the consistency between the predictions of the Cplex-iso-electronic theory and hadronic chemistry is for future study. Hadronic chemistry converges at least 1000 times faster than the present C.I. calculations and thus can deal more accurately with complex systems compared to the present quantum chemical methods. Hadronic chemistry also permits an exact quantitative representation of the chemical bond thus allowing new predictions for pericyclic reactions and aromatic/antiaromatic compounds to emerge.

2. Results and discussion

2.1. Electrocyclisations and ring openings

Applying the ADEP concept to the ring opening of cyclobutene results in the electronic mechanism illustrated in 1, Fig. 1. Based on the logic of this theory the C3–C4 single bond undergoes heterolytic fission in the $1'$ process. The terminus (C-4) with the greatest electron density (DSIED) rotates 90° downwards (as drawn) in a clockwise motion and attacks the C=C bond at C-1. This results in an increase in electron density at the top face of C-2 due to the ADEP process. C-3 (AFS) rotates 90° upwards towards the top face of C-2 resulting in neutralisation of the decrease in electron density at

C-3, formed due to heterolytic fission in the $1'$ process, and thus prevents charge accumulation which lowers the activation energy and avoids formation of an intermediate. The process occurs in a gradual manner, as in cycloaddition reactions [1], to minimize charge accumulation i.e. the $2'$ process occurs before the $1'$ process is completed. This represents a clockwise rotation at C-3 and hence overall conrotatory (rotation in the same direction) motion occurs at the termini. By definition the rotation is asynchronous (semirotatory). Ring opening of cyclobutenes has been shown experimentally to occur in a conrotatory fashion under thermal conditions [4], as predicted by the Cplex-iso-electronic theory. Ring opening has been shown to be unimolecular and insensitive to environmental changes consistent with a concerted pathway. C-3, with its decrease in electron density, cannot rotate first towards and interact with the C=C bond as opposed to C-4 in the $1'$ process as this would result in the two isoelectron pairs moving on the same face of cyclobutene to neutralise charge accumulation, generating severe electronic repulsion. This is valid for all ring openings/electrocyclisations. In the case of cyclobutene the path of the two isoelectron pairs actually cross [1] in this scenario, which further inhibits this electronic mechanism. This logic implies that the AFS in pericyclic reactions can only be stabilised by electron density arising from the ADEP process.

The cyclobutene ring is strained and thus favours synperiplanar dynamics over antiperiplanar dynamics [1]. The lack of an SDEP process in the ring opening of cyclobutene is due to the paths of the isoelectron pairs crossing [1]. The fact that the SDEP process is not involved implies that the efficiency of the ring opening is reduced. The amount of strain will determine the degree with which the ADEP process can compete with the more favoured SDEP process. The less strained the substrate, the more efficient the ADEP process. More published and systematic empirical data on the addition of nucleophiles to strained systems is required to quantify this, especially from substrates with low steric effects. As the single bond breaks in the $1'$ process the strain of the cyclobutene ring decreases and hence the efficiency of the ADEP process increases as the ring opening reaction progresses.

Within this new chemical theory if inversion of the electron density at C-4 occurs in the $1'$ process of the cyclobutene ring opening, the rearrangement is predicted to result in a disrotatory manner. The fact that this does not occur is due to the inversion process destabilizing the $1'$ process. The $1'$ process is predicted to be the major factor in the electronic mechanism [1]. Inversion of the electron density at C-4 (DSIED) involves a separation of charge which decreases the stability of both C-3 and C-4, especially C-3 (AFS) as it interacts with the C1–C2 double bond later than C-4. Furthermore destabilisation of the AFS increases the ability of the AFS to interact with the electron density of the C=C double bond which further destabilises the system as discussed above (first paragraph; Section 2.1). Inversion at C-3 (AFS) would also destabilise the AFS. Retention at both C-3 and C-4 in the $1'$ process insures that both sites stabilize each other until there is a sufficient interaction with the C1–C2 double bond. Retention at the DSIED also means a faster neutralisation of the AFS as inversion adds

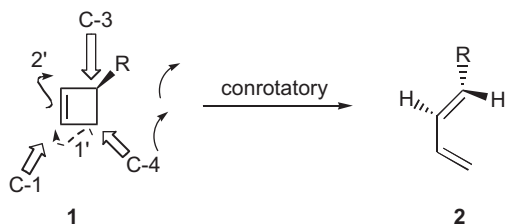


Fig. 1. The ADEP syn FSED electronic mechanism for the concerted ring opening of cyclobutene.

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