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NONREACTIVITY OF RYDBERG STATES WOODWARD–HOFFMANN FORBIDDEN $[2_s+2_s]$ PHOTOCHEMICAL CYCLOADDITIONS

KLAUS WITTEL*
Anorganische Chemie II, Frankfurt University, BRD-6000 Frankfurt, Theodor Stern Kai 7, West Germany

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Abstract—A theoretical analysis is presented for the $[2_s+2_s]$ cyclodimerisation of molecules in which the lowest unoccupied MO is of Rydberg nature. The concerted mechanism is forbidden by the Woodward–Hoffmann rules for the thermal and the photochemical path. However, the frontier MO approach predicts an enhancement of these reactions. Experiments related to this analysis are discussed.

Zusammenfassung—Eine Analyse der Orbitalkorrelationen zeigt, daß die thermische und photochemische $[2_s+2_s]$ Cyclodimerisation nach den Woodward–Hoffmann-Regeln verboten ist für Moleküle mit einem Rydberg-Orbital als unterstes unbesetztes MO. Dagegen zeigt die Grenzorbital-Theorie keinerlei Beeinträchtigungen dieser Reaktionen. Abschließend werden mögliche Beispiele diskutiert.

The importance of molecular Rydberg states[1] is often hidden from the chemist due to the absorptivity of air and of solvents. Population of such states by the techniques of vacuum UV spectroscopy generally induces dissociations and fragmentations of the excited molecule, processes which are of prime interest in the gas phase photochemistry of small molecules.[2] This paper tries to outline the influence of low-lying Rydberg states on the reactivity of medium-sized molecules by using the popular orbital correlation[3] and the frontier molecular orbital[4] approaches. As an example, the $[2_s+2_s]$ electrocyclic dimerisation is analysed. It will be shown that these dimerisations are forbidden by the Woodward–Hoffmann rules for both, thermal and photochemical paths, but that both reactions will obtain considerable enhancement by the frontier orbital approach.

Little is known about photodimerisations of simple alkenes,[5] which prefer isomerisation and fragmentation reactions. Tetramethylethylene yields octamethylcyclobutane on irradiation;[6] 2-butene, aside from isomerisations and fragmentations, dimerises photochemically,[7] as do fumaronitrile[8] and fumaric acid dimethylester.[9] These reactions result in stereospecific products, which in the case of 2-butene suggests a concerted mechanism; the fumaric acid derivatives were investigated in the solid phase, where packing effects may enforce stereospecific products.

After a short description of Rydberg orbitals, an orbital correlation diagram is analysed, and its bearing on some specific molecules, namely fluoroalkenes and methylsubstituted ethylenes, is discussed. Rydberg states are best described utilizing Rydberg orbitals. A Rydberg orbital is large, it encompasses the whole molecule, and the nuclei are well inside the region of the orbital. Because of its size, the Rydberg orbital is labelled by the angular momentum quantum number l; the deviations from spherical symmetry, which are induced by the actual arrangement of the nuclei, are only considered as small perturbations. The R_{3s} orbital of, e.g. ethylene is consequently nearly spherically symmetric in the outer regions. Rydberg states of p, d, ... type also exist. The energies of Rydberg orbitals range from $-4\,eV$ to $0\,eV$, which places the excitation to Rydberg states into the far ultraviolet ($\lambda \leq 250\,nm$) region of the spectrum. More complete discussions of Rydberg spectroscopy are contained in the literature.[1]

Figure 1 presents the orbital correlation diagram for the electrocyclic dimerisation of an alkene in which the LUMO (*L*owest *U*noccupied *M*olecular *O*rbital) is of Rydberg type. The two LUMO combinations correlate with an s-type, R_s, and a p-type, R_p, Rydberg orbital in the united molecule. This correlation diagram is supported by Extended Hückel[10] calculations with a 3s Rydberg orbital on each ethylenic unit,[11] but the calculations do not offer any additional insights.[12] It is obvious that only one of the two HOMO (*H*ighest *O*ccupied *M*olecular *O*rbital) combinations of the monomers correlates with an occupied MO in the cyclodimer, which, in the spirit of the Woodward–Hoffmann rules,[3] implies a forbidden thermal reaction. The two LUMO combinations of the monomers, on the other hand, still correlate with two unoccupied MOs in the cyclodimer. This situation is independent of the specific ordering of the levels within the manifold of unoccupied orbitals in the cyclodimer; this ordering is unknown to a large extent. Consequently, this concerted $[2_s+2_s]$ cyclodimerisation is forbidden both for the thermal and the photochemical route.

If one now leaves the realm of orbitals and starts to think about molecules, on which one could test the predictions of the correlation diagram, the situation becomes more complex:

Photochemical cyclodimerisations of ethylenes are probably hindered by the nonplanar geometry of the $\pi\rightarrow\pi^*$ excited molecules: Ethylene is twisted by 90° in its $\pi\rightarrow\pi^*$ excited state,[13] whereas Rydberg states of alkenes generally are planar[14] like the lowest cationic states;[15] ethylene itself is twisted by about 30° in its R_{3s} state,[16] whereas hardly any distortions are indicated in the Rydberg and photoelectron spectra of halogenated ethylenes. Thus, cycloadditions of $\pi\rightarrow R_s$ excited alkenes should not be hindered for steric reasons.

It must be added that valence/Rydberg exchange integrals are usually small: The lowest triplet state is

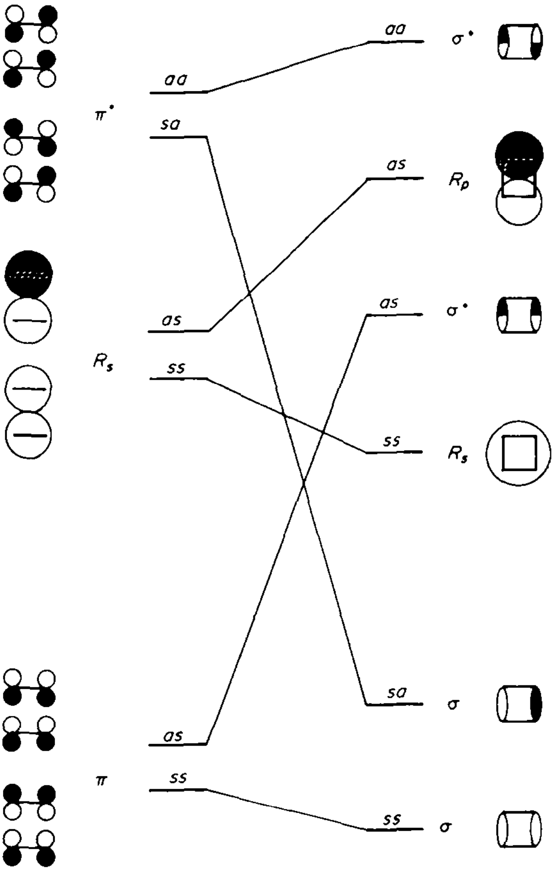


Fig. 1. Orbital correlation diagram for the cyclodimerisation of an alkene, in which the LUMO is of Rydberg nature. The first and second symmetry labels refer to the plane between the two molecules and the mirror plane bisecting both molecules, respectively.

usually of intravalence, $\pi \rightarrow \pi^*$ character, even if the lowest singlet excited state is of Rydberg nature, and well separated from the next one.[17] Therefore, sensitised reactions may well proceed.

There are some molecules in which the lowest excited singlet state is of Rydberg character. These examples comprise heavily alkylated alkenes like tetramethylethylene[18] and perfluorinated alkenes like tetrafluoroethylene[19] or perfluorbutene.[14] In for example tetrafluoroethylene, the $\pi \rightarrow \pi^*$ excitation is beyond 160 nm, whereas the R_{3s} state is around 190 nm.[19] For these molecules, some specific statements concerning concerted cyclodimerisations can be made on the basis of the correlation diagram (Fig. 1):

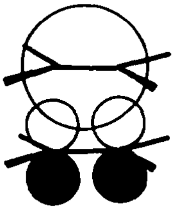
(i) Tetrafluoroethylene should not cyclodimerise in a photochemical ($\lambda > 160$ nm) reaction.

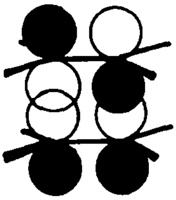
(ii) The photochemical cyclodimerisation of tetramethylethylene should be extremely dependent on the exciting energy. The transition to the R_{3s} state, which is the lowest in energy, immediately precedes the intense $\pi \rightarrow \pi^*$ transition. The latter transition is responsible for the observed photochemical reactivity.[6,22]

(iii) Perfluoroalkenes should resist cyclodimerisation via their lowest singlet excited state, since that is usually of Rydberg character. In line with this conclusion, no cyclodimerisation products were observed in a recent study of the photochemistry of perfluoroalkenes.[20]

These statements do suggest more stringent experimental tests which will be far from simple: The reactions should be tried in the gas phase since Rydberg orbitals are heavily perturbed in condensed media;[1] they require a good tunable light source for wavelengths around 200 nm; and finally, a careful product analysis is necessary to exclude possible dimerisation products. Despite, or rather because of these difficulties does the correlation diagram described here present a challenge to the experimentalist.

Finally, one has to comment on the ease of thermal dimerisation of the fluorinated alkenes, which proceed by a two step, diradical mechanism.[5,21] The correlation diagram does not, of course, apply to this type of reaction, Fukui's frontier orbital approach[4] seems more suited: According to this theory, a reaction path is governed by the nodal properties of the frontier orbitals (HOMO and LUMO) of the reactants. Thus there should be an attractive interaction for the thermal dimerisation of tetrafluoroethylene, where the LUMO is a Rydberg orbital, and a strongly repulsive interaction for ethylene, where the LUMO is the antibonding π^* orbital. This situation is depicted below.





Although overlap between Rydberg and valence orbitals (1) is small, it is still significant for long distances, the π/π repulsion is of a more short range nature. Thus the attractive π/R_s interaction may well provide the necessary stabilization energy in the early stages of the reaction, so that a two step process eventually may become feasible via a diradical intermediate. Finally, it should be stressed that the frontier molecular orbital approach is *not* equivalent to the orbital correlation diagram technique of Woodward and Hoffmann for this specific ordering of levels, whereas both approaches yield identical results for the "normal" case where the LUMO is of π^* nature. Both techniques have to be used in some complementary way in order to describe and possibly understand the problem of chemical reactivity.

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[12] Except perhaps that the Mulliken–Helmholz–Wolfsberg approximation [M. Wolfsberg and L. Helmholz, *J. Chem. Phys.* **20**, 837 (1952); R. S. Mulliken, *J. Chim. Phys.* **46**, 497, 675 (1949)] $H_{ij} = K \cdot S_{ij} \cdot (H_{ii} + H_{jj})/2$ is not suited for the case of large overlap, $S \rightarrow 1$. This can be seen by considering two identical orbitals ($S=1$), the energy of the surviving bonding combination would have an energy of $H \cdot (1 + K)/2$ according to the above approximation instead of H.

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[15] Cf. K. Wittel, W. S. Felps, L. Klasinc and S. P. McGlynn, *J. Chem. Phys.* **65**, 3698 (1976) for a collection of pertinent references.

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[22] The photochemical reaction of tetramethylethylene should also show a pronounced solvent effect, since Rydberg states move to higher energy on going from the vapour phase to paraffinic and to hydroxylic solvents, whereas $\pi \rightarrow \pi^*$ states remain relatively unperturbed. We thank a referee for having drawn our attention to this aspect.