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Funnels and barriers in the photocycloaddition of arenes to alkenes and dienes

Johanna A. van der Hart, Jan J.C. Mulder, Jan Cornelisse
Gorlaeus Laboratories, Leiden University, P.O. Box 9502, 2300 RA Leiden, Netherlands

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Abstract

In the photocycloaddition of benzene to alkenes, products are formed in the ortho and meta addition modes; in the photoaddition of benzene to the terminal atoms of a diene system, products are formed in the meta and para modes. On the basis of orbital symmetry correlations, meta photocycloaddition has been described as an allowed process. The situation regarding the ortho and para modes is less clear. It is shown that orbital symmetry correlations can also be used to predict the occurrence of reactive minima or funnels in the potential energy surface of the first excited state of the reactants. The presence of these funnels can be used to rationalize the abundance of ortho and meta adducts in the photoaddition of arenes to alkenes, and the occurrence of meta and para adducts in the photoaddition of arenes to dienes. The role of charge transfer in the selection of the addition mode and in the regioselectivity in the ortho mode for arenes to alkenes is discussed.

Keywords: Photocycloaddition; Benzene; Alkenes

1. Introduction

The photochemical cycloaddition of arenes to alkenes and dienes has been known for decades. In 1959, Angus and Bryce-Smith [1] reported the ortho photocycloaddition of maleic anhydride to benzene; Wilzbach and Kaplan [2] and Bryce-Smith et al. [3] reported the meta photoaddition of several olefins to benzene in 1966 and, also in 1966, Koltzenburg and Kraft [4] discovered the para photoaddition of benzene to isoprene and butadiene. The retention of the alkene configuration in the photocycloadditions suggests a concerted process [5,6].

The three modes of addition for the photocycloaddition of benzene to ethylene are depicted in Figs. 1–3.

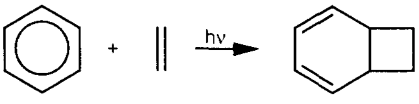

Fig. 1. Ortho photocycloaddition of benzene to ethylene.

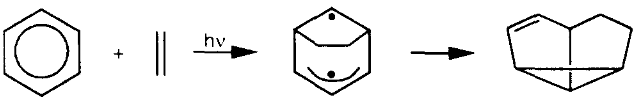

Fig. 2. Meta photocycloaddition of benzene to ethylene.

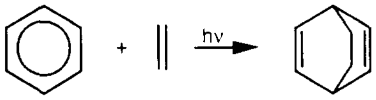

Fig. 3. Para photocycloaddition of benzene to ethylene.

The meta, ortho and para photocycloadditions of benzene to the terminal C atoms of a diene proceed in a similar way.

In the ortho and para addition modes, a plane of symmetry can be assumed during the addition process. For the meta photocycloaddition, a possible route was suggested by Bryce-Smith [7] in which the two σ bonds between the reactants are formed first, leading to the bicyclo[3.2.1]octenyl biradical in the case of the addition of benzene to ethylene. The addition product results from the closure of a three-membered ring. This reaction mechanism is now generally accepted [8]. Experiments and theoretical considerations confirm the assumption that the bonds between the reactants are formed at the start of the addition process [9,10]. Therefore, in this case, a plane of symmetry can be assumed in the first stage of the addition process.

Since in all modes of addition a plane of symmetry can be assumed, molecular orbital and state correlations can be used and the Woodward–Hoffmann [11] rules

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can be applied to investigate whether symmetry-imposed barriers are present during the reaction processes. Bryce-Smith [7] has listed the state correlations between the reactants for the thermal and photochemical reactions; molecular orbital correlation diagrams have also been published [12,13]. For the meta addition mode, a photochemically allowed correlation has been found between the ground state of ethylene or butadiene plus the first excited singlet state of benzene ($^1B_{2u}$) and the ground state of the biradical [7]. For the ortho and para photocycloaddition modes, correlations were considered between the ground state of ethylene or butadiene plus the lowest ($^1B_{2u}$) and second excited ($^1B_{1u}$) singlet states of benzene and the low-lying excited states of the products. The correlations are symmetry forbidden for the $^1B_{2u}$ state and symmetry allowed for the $^1B_{1u}$ state.

Experimentally, meta and ortho adducts are formed in the photoaddition of arenes to alkenes and meta and para adducts in the photoaddition of arenes to dienes. The occurrence of ortho and para adducts has been explained by charge transfer processes [7,14] or by the population of the second excited singlet state of benzene [7,15]. The different behaviour of dienes compared with alkenes cannot be explained by the correlations between the first or second excited state of benzene and the low-lying excited states of the product. However, we show that the occurrence of ortho photoaddition products for benzene and alkenes and para photoaddition products for benzene and dienes can easily be explained on the basis of minima in the potential energy surfaces (PESs) of the first excited states of the reactants, which can act as funnels for the photochemical processes. On the basis of correlation diagrams, we investigate in which addition modes these reactive minima occur, and also look at the barriers in the pathways to the funnels to explain the preference of one addition mode to another. We restrict ourselves to photoadditions in which benzene is the excited species and to pathways in which a plane of symmetry is present. Therefore we use s-*cis*-1,3-butadiene as a representative of the diene systems.

For the photocycloaddition of benzene to an alkene or diene, the degeneracy of both the HOMOs[1] and LUMOs of benzene is a complicating factor. A correlation between a HOMO of the reactants and a LUMO of the addition product and vice versa does not always imply a correlation between the first excited states. Therefore we investigate the role of barriers and funnels in the photochemical processes for reactants with one single HOMO and one single LUMO before we look at the possible funnels in the PES of the first excited state of the system of benzene and an alkene or diene and before we discuss the accessibility of these funnels in the ortho, meta and para modes.

2. Molecular orbital correlation diagrams, energy minima and barriers

On the basis of MO correlation diagrams, Woodward and Hoffmann [16] have shown that, in the case of the photodimerization of ethylene to cyclobutane, the HOMO of the system consisting of two molecules of ethylene is correlated with the LUMO of cyclobutane and the HOMO of cyclobutane with the LUMO of the ethylenes. Therefore an electron configuration with one singly occupied HOMO and one singly occupied LUMO of the reactants corresponds to an electron configuration with one singly occupied HOMO and one singly occupied LUMO of the product, i.e. the first excited state of the reactants correlates with the first excited state of the product. Woodward and Hoffmann [17] assumed that the photodimerization is an allowed process because no symmetry-imposed barrier is present since the lowest excited state of two ethylenes correlates directly with the first excited state of cyclobutane. However, in addition to the correlation between the first excited states, we must take into account the correlation of the ground state of the reactants with a doubly excited state of the product and vice versa for a good description of the photochemical process. According to semi-empirical calculations by van der Lugt and Oosterhoff [18] for the disrotatory ring closure of butadiene to cyclobutene, the doubly excited electronic configuration plays an important role in the photochemical reaction. Similar results have been obtained for the photodimerization of ethylene [19] and the correlation diagrams involved in this case are treated in several textbooks on photochemistry [15,20,21]. In the configuration correlation diagram (see Fig. 4), the ground state electronic configuration of the reactants is correlated with a doubly excited electronic configuration of the product and vice versa. The electronic configurations of the first excited states of the reactants and product are also correlated. After configuration interaction, an avoided crossing between the PESs of the ground state configuration and the doubly excited configuration causes a barrier in the ground state PES and a well in the PES of the excited state. This energy minimum is so deep that it becomes a well in the PES of the first excited state and can act as a funnel for the photoreaction. The state with the doubly excited configuration is the driving force for the photochemical reaction [20,21]. In this theoretical description of the photochemical process by van der Lugt and Oosterhoff [18] a route is provided for the conversion of the excited state reactant to the

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[1] The terms HOMO and LUMO are used for the highest occupied and lowest unoccupied molecular orbitals respectively for a molecule in the ground state and also when the HOMO and LUMO are singly occupied in the excited state.

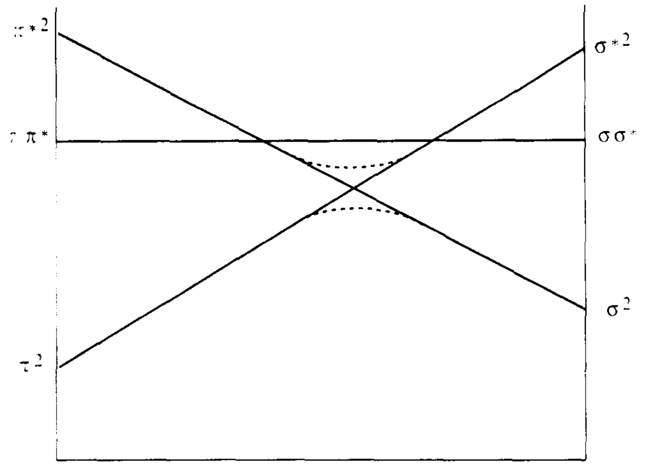

Fig. 4. Electronic configuration correlation diagram for the face-on cyclodimerization of ethylene to cyclobutane; π and π* represent the HOMO and LUMO of the ethylene system and σ and σ* the HOMO and LUMO of cyclobutane.

ground state product; Zimmerman [22] and Dougherty [23] have proposed a similar pathway.

In all cases in which a bonding orbital of the reactant(s) is correlated with an anti-bonding orbital of the product(s), i.e. in all cases in which the thermal reaction is symmetry forbidden, an energy minimum in the PES of the first excited state can be expected. This energy minimum can only act as a funnel for the photoreaction if it is accessible for the reactants. In 1974, Michl [24] discussed the role of barriers in the PES between the starting geometry and the conformation of the reactants in the funnel and showed the relevance of correlation diagrams and the Woodward–Hoffmann rules. If the HOMO of the reactants is correlated with the LUMO of the product and vice versa, two conditions are fulfilled: a funnel will be present and the funnel will be accessible because the energy of the first excited state will change rather smoothly during the reaction process as the decrease in energy of the LUMO is compensated by the increase in energy of the HOMO. Consequently, no energy barrier is expected between the start of the reaction and the funnel; the photochemical process is allowed.

3. Photocycloaddition of benzene to alkenes and dienes

The MO correlation diagrams [12,13] and the state correlations [7] for the photocycloaddition of benzene to alkenes and to the terminal C atoms of dienes for all three modes of addition are known. The MOs of benzene in relation to the addition modes are indicated in Fig. 5.

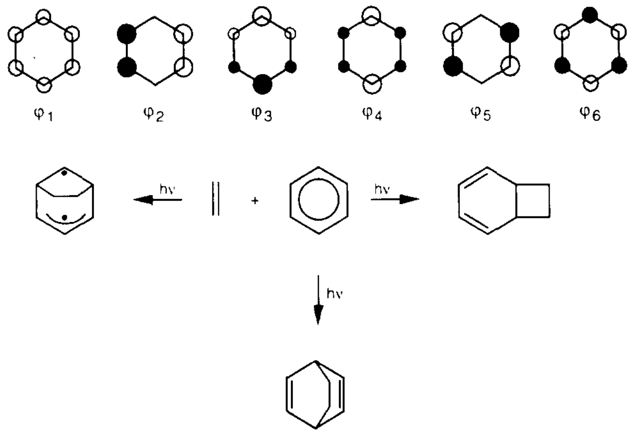

Fig. 5. The molecular π orbitals of benzene in relation to the ortho, meta and para addition modes for the photocycloaddition of benzene to ethylene. The lowest excited singlet state of benzene ($^1B_{2u}$) has the electronic configuration $\phi_2\phi_4-\phi_3\phi_5$; the second excited singlet state ($^1B_{1u}$) has the electronic configuration $\phi_2\phi_5-\phi_3\phi_4$; the electronic configurations of the degenerate excited state $^1E_{2u}$ are $\phi_2\phi_4+\phi_3\phi_5$ and $\phi_2\phi_5+\phi_3\phi_4$ [25].

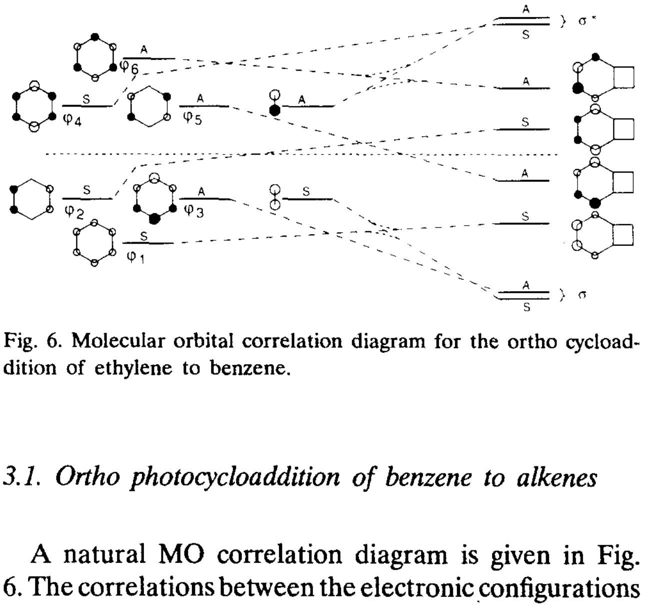

Fig. 6. Molecular orbital correlation diagram for the ortho cycloaddition of ethylene to benzene.

3.1. *Ortho photocycloaddition of benzene to alkenes*

A natural MO correlation diagram is given in Fig. 6. The correlations between the electronic configurations and the states of the reactants and the adduct can be deduced from the MO correlation diagram. The electron configurations $\phi_2\phi_4$ and $\phi_3\phi_5$, both involved in the first excited state of benzene, combined with the ground state electronic configuration of ethylene, correlate with doubly excited electronic configurations of the adduct. The first excited state of the reactants is therefore correlated with a high-lying excited state of the product. On the basis of the latter correlation, the ortho photocycloaddition of benzene to ethylene has to be considered as forbidden [7,15,26] from the $^1B_{2u}$ state. From the MO correlation diagram it also follows that the electronic configuration $\phi_2\phi_5$ of benzene, combined with the ground state electronic configuration of ethylene, correlates with the electronic configuration of the first excited state of the product; consequently, the second excited state of the reactants correlates with the first excited state of the product [7]. The ground state electronic configuration of the reactants correlates with a doubly excited electronic configuration of the product and the ground state electronic configuration of the product corresponds with a doubly excited electronic configuration of benzene plus the ground state configuration of ethylene. On the basis of these correlations, a barrier in the ground state PES and a reactive minimum in the PES of the first excited state can be assumed

The occurrence of a reactive minimum in the PES of the first excited state makes the ortho photocycloaddition an allowed photoreaction for arenes to alkenes if the minimum is accessible. Because the first excited state of the reactants correlates with a high-lying excited state of the product, we must assume that the reactants have to overcome a barrier of considerable size before reaching the funnel. On the basis of the electronic configuration correlations, we also know that the second excited state correlates with the first excited state of the product; the crossing between these states of different symmetry decreases the barrier. A state correlation diagram is given in Fig. 7(a); this correlation diagram is similar to the diagram of Michl and Bonačić-Koutecký [27] given for a ground state forbidden reaction with an "abnormal" MO crossing. In our case it is also possible that the doubly excited electronic configurations, which are involved in the avoided crossing leading to the funnel, mix with the electronic configurations of the first excited state of benzene in an early stage of the reaction process as they have the same symmetry (see Fig. 7(b)). In addition, charge transfer between the reactants at the start of the reaction will lower the assumed barrier. Therefore we suppose that the barrier will be of moderate size. We discuss the role of charge transfer on the height of the energy barrier between the start of the reaction process and the reactive minimum in Section 5.

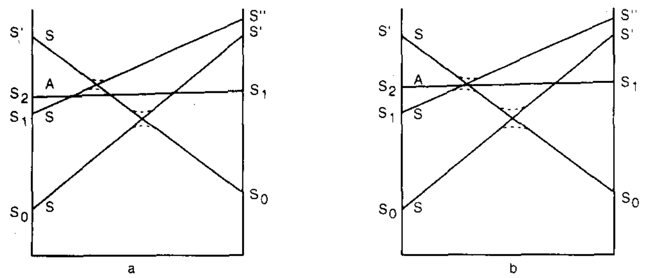

Fig. 7. State correlation diagrams for the ortho photocycloaddition of benzene to ethylene. S_0, S_1 and S_2 denote the ground state and the first and second excited states; S′ and S″ indicate high-lying doubly excited states. The relative position of S_2 with respect to S_1 and the interaction between the symmetric singly excited state and the doubly excited states determine which electronic configuration(s) will dominate in the first excited state of the reactants on the pathway from the start of the photoaddition to the funnel. Two possibilities are given in (a) and (b).

3.2. *Ortho photocycloaddition of benzene to dienes*

For the ortho cycloaddition of benzene to s-*cis*-butadiene, the electronic configurations of the ground states of the reactants and product are correlated [7]. In this case no avoided crossings leading to a potential well in the excited state can be expected; no driving force for a photochemical reaction is present. In the literature [7,13] this photoaddition process is considered to be forbidden from the $^1B_{2u}$ state of benzene and allowed from the $^1B_{1u}$ state on the basis of state correlations. In our opinion the lack of a reactive minimum determines the outcome. As far as we know no ortho adducts are formed in the photocycloaddition of dienes to arenes.

3.3. *Para photocycloaddition of benzene to alkenes*

For the para addition of benzene to alkenes, the electronic configurations of the ground states of the reactants and product are correlated [7] and therefore no reactive minimum in the first excited state can be expected. Experimentally, para adducts have only been found in a few cases. Wender et al. [28] have mentioned some para products of arenes and alkenes in a review of arene–alkene photocycloaddition; one of these products, resulting from the intermolecular photoaddition of phenethyl vinyl ether [29], has recently been re-investigated and found to be a secondary product (not a para adduct) formed by the rearrangement of an initial meta adduct [30]. Mirbach et al. [31] have found a para adduct as a secondary product in the photochemical cycloaddition of ethylene to benzene.

3.4. *Para photocycloaddition of benzene to dienes*

As for the ortho addition of benzene to ethylene, a doubly excited electronic configuration of the reactants is correlated with the ground state electronic configuration of the product and a funnel can be expected in the reaction path. Experimentally, para adducts have been found [4,32–34]. Since the combination of the first excited state of benzene and the ground state of s-*cis*-butadiene is correlated with a high-lying state of the addition product [7], the 1,4–1,4 photocycloaddition of benzene to 1,3-dienes is considered to be forbidden for the $^1B_{2u}$ benzene state. We prefer to consider this photoaddition as an allowed photoreaction, as in the ortho addition of benzene to an alkene, on the understanding that the barrier will be of moderate size.

3.5. *Meta photocycloaddition of benzene to alkenes and dienes*

Bryce-Smith [7] has shown that the meta photocycloaddition of benzene to alkenes and dienes via a biradical species is allowed because the antisymmetric first excited state of benzene and the ground state of ethylene or s-*cis*-butadiene are correlated with the lowest singlet state of the biradical adduct. MO correlation diagrams for the meta addition of benzene to ethylene [12,13] and natural MO correlation diagrams for the addition of benzene to ethylene and s-*cis*-1,3-butadiene [35] are known. Semi-empirical [10] and ab initio [36] calculations confirm the existence of a crossing between the PES of this antisymmetric state and a symmetric state resulting from the ground states of the reactants in the addition of benzene to ethylene. Because both states differ in symmetry there is a real crossing. Experimentally, many meta adducts are found. The meta photocycloaddition of arenes to alkenes has recently been reviewed by Cornelisse [37]. Photoadducts of benzene to the terminal C atoms of diene systems have been described by Berridge et al. [33] and Cantrell [34].

4. Symmetry and the location of the minima

Experimentally, ortho and meta addition products are found in the photocycloaddition of benzene to alkenes and meta and para adducts in the photoaddition of benzene to dienes. These results are in full agreement with the presence of reactive minima in the PES of the first excited state in the addition modes. Orbital symmetry correlations thus provide an insight into the possibility of a photochemical reaction. However, these correlations are not conclusive with respect to the preference of a symmetric path over an asymmetric path. We must consider the consequences for the location of the minima if symmetry is no longer present.

For the meta photocycloaddition, the crossing of the PES of the symmetric ground state and the antisymmetric first excited state is a real crossing in a symmetric pathway. If the symmetry constraints are released, the mixing of both states will lower the ground state energy and raise the energy of the excited state. Therefore we assume that the crossing is a minimum on the PES of the first excited state and a real funnel for the reaction.

For the ortho photocycloaddition of benzene to alkenes, the avoided crossing between the symmetric ground state and the symmetric doubly excited state causes a dip in the PES of the first excited state. There is an energy gap between this state and the ground state; it is not excluded a priori that the release of symmetry constraints will diminish this energy gap by configuration interaction, e.g. with configuration(s) correlated with the singly excited states of the reactants. For the 2+2 dimerization of ethylene, a reaction similar to the ortho cycloaddition of benzene to ethylene, Bernardi et al. [38] have found two conical intersections in the PESs of the ground and first excited states. The conformations belonging to the apices of these intersections deviate from the highly symmetric rectangular geometry for a symmetric pathway. The same results can be expected for the ortho photocycloaddition which is also a 2+2 cycloaddition.

Also, in the para photocycloaddition of benzene to dienes, an avoided crossing in a symmetric pathway is present, and so we may expect a dip in the PES of the first excited state. Also, in this case, the possibility of real funnels situated on the PES of the first excited state in an asymmetric conformation cannot be excluded.

For the ortho photocycloaddition of benzene to dienes and the para photocycloaddition of benzene to alkenes, the ground states of the reactants and products are correlated. The energy gap between the PES of the ground state and the first excited state will be large along the reaction path and we may expect that the release of the symmetry constraints will not change this picture to a large extent.

5. Relative accessibilities of the minima

The photocycloadditions are very selective, e.g. the addition of benzene to alkenes shows selectivity towards the meta or ortho addition mode. Pronounced regioselectivity in the meta mode and smaller regioselectivity in the ortho mode, as well as stereoselectivity in both modes, are found. In order to obtain a better insight into the selectivity, we must inspect the depth and position of the reactive minima leading to each of the products and the barriers between the starting point of the reaction process and these minima. On the basis of the high symmetry of the benzene ring, several locations on the PES are possible for the minima. For the meta photocycloaddition to ethylene there are six possibilities, and for the ortho addition at least six, but this number is probably doubled if the conformation in the reactive minimum is not symmetric as in the case of the dimerization of ethylene. For monosubstituted benzenes, the six minima in the meta addition are no longer equivalent; the minima will differ in depth and width for the ipso,meta, ortho,para, meta,meta and ortho,ortho modes, and also the heights of the barriers in the pathways to the funnels will differ. For ethylenes with a substituent at the double bond, the position of this substituent can be endo or exo with respect to the benzene ring. On the PES of the first excited state in the meta and ortho photocycloadditions of arenes to alkenes, and in the meta and para photocycloadditions of arenes to dienes, we may therefore expect a large number of local minima separated by barriers. Only the accessible minima can act as funnels for the photochemical reactions and their relative accessibility determines the selectivity.

In the case of charge transfer in the early stage of the reaction process, the interaction between the reactants can be treated as the interaction between the zero-order wavefunctions for the reactants and the zero-order wavefunctions for the charge transfer complexes. Beens and Weller [39] used this method for excited molecular π complexes, and described the interaction between the locally excited and the donor–acceptor complexes; their method can be employed for exciplexes, and also for calculations of the relative heights of the potential energy of the reactants in the several pathways to the possible funnels in the PES.

If charge transfer is negligible, the first-order interaction will be weak and is determined by the mutual overlap between the HOMOs and LUMOs of the reactants. In this case we expect that the meta mode of addition will be favoured with respect to the ortho mode on the basis of the assumed heights of the barriers in these pathways. Indeed, experimentally, meta photocycloaddition is found for arenes and alkenes which do not differ greatly in electron donor characteristics. The method of Beens and Weller [39] has been employed to explain the regioselectivity found in the meta photocycloaddition of monosubstituted benzenes to alkenes and dienes [35]; a frontier orbital method has been used by Houk [40] in the case of the photoaddition of substituted benzenes to alkenes.

If charge transfer dominates the interaction, the contribution of the electronic configuration of the charge transfer complex to the electronic configurations of the first excited state lowers the potential energy to a large extent, and the electron probability density in the reactants is changed with respect to that observed for photoadditions between reactants which do not differ greatly in electron acceptor or donor characteristics. In this way, the influence of charge transfer is very important for the course of the PES during the addition process from start to funnel. Assumed barriers become less high and the pathways to funnels which were inaccessible without charge transfer become passable. The charge transfer will also influence the relative orientation of the reactants at the start of the reaction. Coulombic forces will determine the preferred orientations of the reactants and determine the mode of addition and the regioselectivity. The preferred relative orientations of the reactants can be deduced from the charge density distributions in the charge transfer complex. To obtain an idea of the charge distribution in these complexes, we can look at the charge distribution in the arene ions. For monosubstituted benzenes, the charge of positive and negative ions is largely located at the C atom at which the substituent is attached and to a lesser extent at the para C atom. The conformations of the charge transfer complex in which the C atoms of the alkene double bond are in the neighbourhood of either the ipso C atom or (to a lesser extent) the para C atom of the monosubstituted benzene will be preferred.

These theoretical considerations are in full agreement with the results of experiments. Bryce-Smith et al. [41] reported that ortho addition dominates in the case of photochemical cycloadditions of benzene to olefins having either marked donor or acceptor properties; Mattay [42] found an experimental rule for the ratio of ortho to meta cycloaddition of arenes to alkenes based on the Rehm–Weller equation of electron transfer. Mattay's rule points out the importance of electron transfer for the mode of addition in a quantitative way. The regioselectivity can also be rationalized by the preferred orientations at the start of the addition process. From the charge distribution in the reactants at the start of the addition, we can predict that the major addition product from a monosubstituted arene and an alkene will contain a σ bond between an alkene C atom and the C atom in the benzene ring to which the substituent is attached. Indeed, in the ortho photocycloaddition, the favoured orientation appears to be the ipso,ortho mode; in some cases products are also formed in the meta,para mode [43].

The selectivity of the addition mode in the addition of benzene to dienes is less clear. The situation is more complex than for addition to alkenes; the reaction can afford, besides 1,4–1,4 and 1,3–1,4 adducts, 1,2–1,2 and 1,3–1,2 adducts, and the influence of the experimental conditions is large. Cantrell [34] has reported that, in the case of the irradiation of mixtures of benzene and furan, the ratio of the products depends greatly on the various experimental variables, including the relative concentrations of the two reactants, the irradiation time, the light wavelength employed and the intensity of the light source. We presume that the manifold of barriers and funnels, in the limited region of configurational space, levels the PES; as a result the differences between the barriers become small and the accessibility to the different funnels can change with small variations in the experimental situation.

6. Conclusions

Following the Woodward–Hoffmann rules, the para and ortho photocycloaddition of benzene to alkenes and dienes is considered to be forbidden from the $^1B_{2u}$ state of benzene and allowed from the $^1B_{1u}$ state. Therefore, the distinction between the ortho photoaddition to alkenes and the para photoaddition to dienes, which both result in addition products, and the para photoaddition to alkenes and the ortho photoaddition to dienes, which do not result in addition products, cannot be understood by considering exclusively state correlations between the low-lying excited states of the reactants and products. However, if we also pay attention to the presence or absence of a crossing between the HOMO or HOMO − 1 of the reactants and the LUMO or LUMO + 1 of the product and vice versa, we see that photoaddition products are formed if these crossings occur. In cases in which the addition is thermally forbidden, the photoreaction is in principle possible via a funnel in the PES of the first excited state; the correlations between low-lying excited states can be helpful to study the accessibility of the funnel. The occurrence of meta and ortho adducts and the lack of para adducts in the photoaddition of arenes to alkenes can be explained by the presence or absence of reactive minima in the PES of the first excited state of the reactants; the occurrence of meta and para adducts and the lack of ortho adducts in the addition of arenes to the terminal atoms of dienes can be explained in a similar manner. The competition between the modes of addition is determined by the accessibility of the funnels.

Our theoretical considerations are also in agreement with the well-known role of charge transfer in the selectivity of the addition mode of substituted benzenes to alkenes, which has been made clear in a quantitative manner by Mattay [42]. The influence of charge transfer in the ortho photoaddition of arenes to alkenes has been the basis for the assumption of an exciplex mechanism for this mode of addition. However, an exciplex mechanism does not differentiate between the ortho and para modes of addition. The suggestion [26] that para addition also probably occurs via an exciplex, as does ortho addition, ignores the importance of the absence of a funnel in the latter reaction process. Our rationalizations imply a reduction in the heights of the barriers on the way to the funnels in the ortho addition of arenes to alkenes by the influence of charge transfer; this reduction can lead to exciplex formation, but does not necessarily lead to an energy well in the PES. These assumptions are also in full agreement with experiments: exciplex emission has been observed in only a few cases [37].

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