

University of Groningen

Excited state charge separation in symmetrical alkenes

Zijlstra, Robert Wiebo Johan

IMPORTANT NOTE: You are advised to consult the publisher's version (publisher's PDF) if you wish to cite from it. Please check the document version below.

Document Version

Publisher's PDF, also known as Version of record

Publication date:
2001

[Link to publication in University of Groningen/UMCG research database](#)

Citation for published version (APA):

Zijlstra, R. W. J. (2001). *Excited state charge separation in symmetrical alkenes*. s.n.

Copyright

Other than for strictly personal use, it is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), unless the work is under an open content license (like Creative Commons).

The publication may also be distributed here under the terms of Article 25fa of the Dutch Copyright Act, indicated by the "Taverne" license. More information can be found on the University of Groningen website: <https://www.rug.nl/library/open-access/self-archiving-pure/taverne-amendment>.

Take-down policy

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

Downloaded from the University of Groningen/UMCG research database (Pure): <http://www.rug.nl/research/portal>. For technical reasons the number of authors shown on this cover page is limited to 10 maximum.

Summary

Alkenes are carbohydrates comprising a carbon-carbon (C-C) double bond. The presence of this double bond causes the majority of alkenes to only have limited intramolecular flexibility. For most alkenes, the rotation around the double bond requires large amounts of energy, causing their primary structure to be caught in a planar form at room temperature.

This picture changes drastically when the double bond is temporarily reduced to a single bond under the influence of light with an appropriate wavelength (photo-excitation). This lifts the molecule from its ground state to a so-called electronically excited state, in which an electron is migrated from the double bond to a higher electronic orbital. The alkene exhibits a much smaller rotation barrier for the aforementioned C-C bond in this excited state, and as a result the planar form of the alkene rapidly changes into a form in which the fragments on either side of the C-C bond approximately adopt a 90° (perpendicular) orientation with respect to each other, instead of the original 0° angle in the planar form.

A peculiar phenomenon that occurs during the twisting process from 0° to 90° is that near the 90° point two electronically excited states meet each other. In principle, the two electrons previously forming the double bond can choose which of the two states they want to occupy. This choice is not unrestricted, though. In a symmetrical molecule they will be equally divided over both states, thus maintaining the symmetry in the charge distribution of the molecule. However, if the symmetry of the molecule is somehow disturbed, both electrons migrate to one side of the molecule. This causes an excess of electrons on one side of the molecule, i.e. the molecule has become 'suddenly polarized'. This phenomenon is frequently referred to as charge separation as well, since one half of the molecule has become positively charged, whereas the other half has become negatively charged.

The work described in this thesis has focussed on the topic of this charge separation process in symmetrical alkenes, and in particular on what kind of symmetry breaking has to be held responsible for the occurrence of charge separation. The motivation for this investigation has been twofold.

In the first place, there is a distinct possibility that this charge separation plays an important role in many photo-excitation processes involving alkenes, like the process of vision in humans and other mammals. This process is initiated by the absorption of a photon by the alkene retinal, which forms an integral part of the eye protein rhodopsin. It is believed that the occurrence of charge separation in retinal may play an important role in the transfer of the electric signal to the brain that ultimately leads to vision.

In the second place, there exists some controversy about the actual cause of the existence of charge separation in symmetrical alkenes. At the end of the seventies a number of quantum chemical studies have been performed on the parent alkene ethylene (C₂H₄). These calculations showed that selective deformation of one half of the molecule in the vicinity of the 90° orientation leads to significant charge separation in the ethylene excited states. In fact, the ethylene proved to be more stable in its charge separated deformed geometry than in its nonpolarized symmetrical form. These findings have led to the belief that such intramolecular deformations are the general driving force behind the

occurrence of charge separation in alkenes. At this point, it is important to stipulate that, if this assumption is correct, the excited states of alkenes should always exhibit charge separation behaviour around the 90° orientation.

Experiments, in which the excited state behaviour of significantly larger alkenes like tetraphenylethylene (TPE) in solution has been investigated, show a different picture. These experiments demonstrate that charge separation strongly occurs in polar solvents, i.e. solvents that exhibit a polarized electron distribution themselves. In nonpolar solvents, i.e. solvents with a symmetrical charge distribution, the occurrence of charge separation is much less pronounced. Therefore, these measurements suggest that the solvent plays a role in the induction of charge separation in such alkenes. This is in disagreement with the outcome of the aforementioned quantum chemical calculations on ethylene, which suggested that charge separation will always take place because it is an energetically favourable intramolecular process in which the solvent plays no role.

It has been the goal of the study presented in this thesis to discover the true driving force behind the charge separation in symmetrical alkenes. This has been done by applying several quantum chemical computational methods, which have been described in the chapters 2-4. Furthermore, an ultrafast spectroscopical technique (time resolved femtosecond pump-probe spectroscopy) has been applied to study the excited state behaviour of a number of symmetrical alkenes in various solvents. The outcome of these studies can be found in chapters 5 and 6.

In chapter 2, CASPT2 calculations (a particular quantum chemical computation method) have been applied to make a comparison between the selective deformation of ethylene and the somewhat larger tetramethylethylene (TME). Although the CASPT2 method is not the most suitable method to study such charge separation processes, it was still selected because more suitable alternative methods were unavailable. It was found that the results of the aforementioned quantum chemical studies on ethylene could be accurately reproduced; the selective deformation of ethylene indeed yielded a more stable, charge separated excited state in the vicinity of the 90° orientation. However, this was not the case for TME; the larger methyl groups proved to introduce such an increase in steric hindrance during selective deformation that it destabilized the charge separated excited states of interest on progressive deformation. These results strongly suggest that for larger alkenes the symmetry breaking by means of intramolecular deformation is an energetically unfavourable process, which implies that this process cannot be held solely responsible for the occurrence of charge separation in symmetrical alkenes.

Having established this, it has been attempted to establish by means of quantum chemical calculations whether solvents are capable to disturb the symmetry of the symmetrical alkenes to such an extent that charge separation can occur. For these studies, the Direct Reaction Field (DRF) Model, which has been developed in Groningen within the group of Van Duijnen, has been used.

In chapter 3 the outcome of an exploratory study using this model has been described. In this study, the C-C bond of undeformed ethylene has been rotated in a stepwise fashion over a range of $70-90^\circ$ in several non-symmetrical surroundings existing of point charges with varying charges. These calculations show that charge separation strongly occurs in the vicinity of the 90° orientation with a maximum occurrence at approximately 81° , but that in the case of small point charges the charge separation in ethylene quickly vanishes beyond this point.

In chapter 4, the findings of a more elaborate DRF study have been reported. In this study, the ethylene has been fixed at its 81° twist angle and has been surrounded by a solvent modeled by 50 molecules in such a way that the solvent is in equilibrium with a symmetrical charge distribution of the ethylene. This way, 20 different solvent configurations were generated, and for each configuration the induced charge separation in the ethylene excited states has been calculated. This procedure has been repeated for five different solvents with varying polarity. The findings of this study proved to be highly interesting. Both nonpolar solvents ethane and tetrachloromethane were unable to induce significant charge separation in the ethylene excited states. In contrast, the weakly polar chloroform as well as the strongly polar acetone and carbon dioxide induced large charge separations in the ethylene excited states. However, the charge separation was less pronounced in the case of chloroform than it was in the other two polar solvents. More importantly, all three polar solvents significantly stabilized the charge separated state.

The here presented theoretical studies strongly suggest that it is more likely that the symmetry breaking, which is a prerequisite for the occurrence of the sudden polarazation in the excited states of symmetrical alkenes, is provided by a (polar) solvent rather than an intramolecular deformation, which is in disagreement with aforementioned theoretical findings of the late seventies.

To investigate these new insights, a spectroscopic experiment at femtosecond (i.e. 10^{-15} s) time scales has been performed, in which the excited state behaviour of TPE in four different solvents has been studied. The findings of this study can be found in chapter 5. These experiments show that during the first picosecond, the C-C bond is significantly elongated, and that this process is mainly solvent independent. At longer time scales, however, the solvent has a marked influence on the TPE excited state behaviour. Most interestingly, the TPE excited state exhibits a strong absorption at 500 nm in polar alcohols. This absorption is much weaker in the nonpolar cyclohexane. This particular absorption has been assigned to the charge separated state of TPE. In addition, by means of fitting the experimental data to a kinetic model, it has been demonstrated that in cyclohexane an equilibrium exists between two TPE excited states in the vicinity of the 90° orientation, which seems to suggest the occurrence of both aforementioned electronic states. Therefore, these experimental findings confirm the outcome of the theoretical studies presented in chapters 2-4, which suggested the solvent to be the driving force behind the occurrence of charge separation in symmetrical alkenes.

Finally, the same experimental technique has been used to study a number of *para*-functionalized TPEs. The outcome of these studies have been reported in chapter 6. In this work, the influence of small functional groups attached to the TPE backbone on the charge separation in the modified molecules is investigated, with the obvious restriction that the addition of these groups did not disturb the overall symmetry of the modified TPEs. The behaviour of four different functionalized TPEs has been studied in both ethanol and cyclohexane. Like in the case of unfunctionalized TPE, hardly any influence of the solvent was observed during the first picosecond. At longer time scales, all four functionalized TPEs showed similar behaviour to TPE in cyclohexane, but in ethanol, wherein the charge separated state can be effectively formed, large differences could be observed. Not only did the investigated functionalized TPEs exhibit large differences in molecular mobility, but the extent of the charge separation also showed large variations between the various compounds. These results prove that molecular modifications are

indeed capable of influencing the dynamic behaviour and the extent of charge separation of such alkenes, although a clearcut correlation between the electronic nature of the substituents and the extent of the charge separation could not be established.