Conical intersections as a mechanistic feature of organic photochemistry

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Abstract:

The photochemical decay channel is the central point of a photochemical mechanism. The traditional view of the mechanism of a photochemical reaction assumes that the excited state reaction path is similar to the ground state path and the decay channel corresponds to an avoided crossing minimum (van der Lugt and Oosterhoff model). In contrast, we find that there is no evidence for a decay path via such an avoided crossing minimum and that excited state reaction paths are very different from those on the ground state. Rather, the photochemical decay channel corresponds to a conical intersection point and plays the central role in mechanistic photochemistry.

The nature of the conical intersection point and its mechanistic implications will be discussed for 3 illustrative types of photochemical reactions (2+2 cycloadditions, polyene electrocyclization/isomerisation, and the di-π-methane rearrangement).

Introduction

The idea of a mechanism in organic chemistry is usually taken to refer to a sequence of structures through which the system passes on the route between reactants and products. Such structures may be minima, transition states, or merely convenient reference points on the reaction path. Modern quantum chemical molecular modelling methods can provide detailed information on the geometries and energetics, not only for the lowest energy reaction paths, but also for higher energy reaction paths that may not be observed experimentally. Photochemical reactivity presents a particularly interesting problem from a mechanistic point of view because the mechanism of a photochemical reaction must involve at least two stages. During the first stage, which occurs on the excited state, the system evolves from the Franck-Condon region via transition states and intermediates to a point (the reaction funnel [11]) where decay to the ground state takes place. After this decay the system relaxes on the ground state potential energy surface by following one or more distinct pathways leading to stable structures. Modern spectroscopic methods provide detailed information on the nature of the excited state reaction path while traditional "wet" chemistry provides information on product distributions and quantum yields. Using quantum chemical methods one can derive information (see for example references[2-17]) from modelling that complements the experimental information through the study of both the excited state and the ground state branches of the reaction and the nature of the decay channel connecting them.

The photochemical decay channel is the central point in a photochemical mechanism. The traditional view of the mechanism of a photochemical reaction assumes that the excited state reaction path is similar to the ground state path and the reaction funnel [1] corresponds to an avoided crossing minimum (van der Lugt and Oosterhoff model[18]). As a result of detailed computations on many photochemical reactions [2-17] we find that there is no evidence for a decay path via such an avoided crossing minimum and that excited state reaction paths are very different from ground state paths. In a polyatomic system the "non-crossing rule" loses its validity and two electronic states of the same spatial/spin symmetry may cross at a conical intersection [19-25]. The photochemical decay channel, thus corresponds to a conical intersection point and plays the central role in mechanistic photochemistry. Our purpose in this paper is to discuss the concept of the conical intersection as the focal point of photochemical mechanisms. We begin with a brief discussion of the general nature of photochemical mechanisms and then proceed to illustrate these ideas with 3 examples from recent computations.
The photochemical decay channel: van der Lugt and Oosterhoff model versus real surface intersections

The mechanistic pathways for a photochemical transformation involving two potential surfaces (of the same symmetry) can be conveniently illustrated using figure 1.

Following light absorption, the reactant A may arrive in the Frank-Condon region B. The system can then return to the ground state via fluorescence, or evolve on the excited state in a photochemical reaction. The mechanism must then involve three parts: evolution on the excited state surface, decay to the ground state surface, and finally evolution to products on the ground state surface. If the system evolves on the excited state (via transition states C and F) to the product region G followed by radiative return to the ground state the reaction is adiabatic in nature (i.e., it takes place essentially on a single electronic state). If the system decays non-radiatively to the ground state at some stage, then the reaction is non-adiabatic (i.e., it takes place on two potential energy surfaces).

![Fig. 1 Schematic representation of the interplay between ground and singlet excited state potential energy surfaces.](image)

Many photochemical reactions are very fast and are essentially concerted so the non-adiabatic mechanism is very common. Non-radiative decay is traditionally assumed \[18\] to occur at an avoided crossing minimum (D-E in fig. 1). The other possibility is that there is a real crossing J which is called a conical intersection \[19\]. In the latter case, the surface crossing will obviously occur very fast, i.e., on the time scale of a molecular vibration. In the former case, the system will have a finite lifetime in the excited state well D before radiationless decay can occur. Until very recently, real crossings J were assumed to be very rare and only a few instances had been reported in theoretical computations. Over the past few years, this situation has changed dramatically and many instances of conical intersections have been documented in our own work and that of others \[2-17\]. Further, these crossing points can now be characterized with the same accuracy as transition states\[26-31\].

Part of the difficulty with photochemical mechanisms is the commonly held view (Fig. 2 the van der Lugt and Oosterhoff model \[18\]) that the reaction path on the excited state is similar to the ground state. In this model, the spectroscopically excited S\(_1\) state crosses with a covalent excited state S\(_2\) very early in the excited state reaction path. Later in the reaction path, the avoided crossing that generates the ground state transition state is assumed to create a "well" on the excited state. This "well" forms the funnel\[1\] where the radiationless decay takes place (see D in fig. 1).

There are two problems with this model: a) the probability of decay through a gap may be very small indeed; b) in a polyatomic system the "non-crossing rule" loses its validity and two electronic states of the same spatial/spin symmetry may actually cross at a conical intersection (and this crossing may...
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Energy

Funnel

Fig. 2 van der Lugt and Oosterhoff model of the photochemical funnel

Fig. 3 A transition state (a) and a conical intersection (b and c) in two geometrical co-ordinates

be far removed from the geometry of the ground state reaction path. The probability of radiationless decay via a surface hop is given as

\[
P = \exp\left(-\frac{\xi}{4}\right)
\]

where \(\xi\) is the Massey parameter given as

\[
\xi = \frac{-E(q)}{2\pi |q| g(q)}
\]

and \(q\) is a vector of nuclear displacement co-ordinates. The term \(g(q)\) is the non-adiabatic coupling matrix element (corresponding to the coupling of nuclear and electronic motion) while \(q\) is the magnitude of the velocity along the reaction path and \(\Delta E\) is the energy gap. Making reasonable assumptions about the velocity and the non-adiabatic coupling, one can demonstrate[19] that unless \(\Delta E\) is less than about 2 kcal mol\(^{-1}\), the decay probability is vanishingly small. But the energy gap at the transition state in organic reactions is about 50 kcal mol\(^{-1}\) so this mechanism cannot operate. However, as we approach a point where the surfaces cross, the decay probability would become unity and a fully efficient decay process is possible. While it is usually assumed that this real crossing cannot occur because of the "non-crossing" rule, this rule only holds for diatomic systems [20-22]. Although this fact has been known since 1929, it was assumed that such real crossings were very rare. In fact such crossings have now been demonstrated to be a common occurrence[2-17]. The most significant point is that the real crossings occur at unusual, but accessible, geometries that lie far from the ground state reaction path. Thus the mechanism of many photochemical reactions must be very different from the commonly assumed one from two points of view: a) the sequence of structures that map out the reaction path has no simple relationship to the ground state reaction path and b) the focal point of the reaction mechanism is not an avoided crossing minimum but rather a real crossing where fully efficient radiationless decay can take place.

Before looking at some examples let us conclude this section with a brief discussion of a conical intersection by analogy with a transition state for a thermal reaction. The topology of the potential surface at a transition state and at a conical intersection is illustrated below (Fig.3)

The transition state (a) is characterized by two geometric co-ordinates \(X_1\) and \(X_2\). The energy is a minimum in \(X_2\) and a maximum in \(X_1\), which is parallel to the reaction path (bold arrow) direction. The transition state thus divides the domain of the reactants from the products. The conical intersection is also characterized by two directions \(X_1\) and \(X_2\). (These directions are well defined and are discussed in reference 28). The potential energy surfaces cross at the apex of the cone. Accordingly, motion in the directions \(X_1\) or \(X_2\) lifts the degeneracy that occurs at the apex of the cone. Whereas the transition state divides the reactants and products on the ground state, the conical intersection divides the excited state reaction path and the ground state reaction path. Notice that there are many possible reaction paths that can pass through the conical intersection whereas the reaction path for the ground state is uniquely defined. At a conical intersection, the reaction path on
the ground state bifurcates and all the possible paths (for infinitely slow motion) lie in the $X_1 \times X_2$ plane. The preceding definitions are easily generalized to many dimensions. The transition state has many other co-ordinates of the type $X_1$ and the energy is a minimum in these co-ordinates. In contrast, the apex of the cone becomes a $n \times 2$ dimensional hyperline and it is possible to find the lowest energy point on this hyperline [31]. The excited state decay should take place in the region of this minimum.

Thus the focal point of a non-adiabatic photochemical reaction is one or more conical intersections (fig. 1 J) This point divides the excited state reaction path from the ground state reaction path. While the conical intersection is not the "kinetic bottleneck" of the reaction (since decay is fully efficient and would take place within a single vibration), it does form a type of "bottleneck" since all reaction paths must pass via this point. The accessibility and the structure of the PE surface in this region must determine the course of the photochemical reaction. It now seems unlikely that avoided crossings (Fig.1 D-E) have a significant role to play in photochemical mechanisms.

Some illustrative examples

We shall now illustrate some of the ideas presented above with some simple examples based on computations that we have carried out recently. The [2+2] singlet cycloaddition of two ethylene molecules and the electrocyclic reaction of butadiene provide the "text-book" examples that can be used to clarify many ideas. In each case the "forbidden" thermal reaction path is supposed to be associated with a strongly avoided crossing of the type shown in fig. 2. In the third example, the di-$\pi$-methane rearrangement, we discuss a different situation which shows how the traditional mechanism for this reaction (a sequence of structures which serve as reference points) is related to a non-adiabatic reaction path with a conical intersection focal point.

Let us begin by considering the topology of the potential surfaces for the [2+2] cycloaddition of two ethylene molecules. These surfaces are given in detail in reference [3] and we will be content with a crude sketch given in fig. 4. The potential surface topology in the region of the "forbidden" anti-aromatic transition state shows the expected anti-aromatic pericyclic minimum A on

Fig. 4 Topology of the $S_1$ and $S_0$ potential surfaces in the region of the "forbidden" anti-aromatic transition state A-B.

a) the geometric variables are $R$ the interfragment separation and a distortion that forms one new C-C sigma bond (le allows the formation of the biradicaloid C)

b) the geometric variables are $R$ the interfragment separation and a rhomboid distortion

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the $S_1$ surface as expected from the Van der Lugt Oosterhoff model. The corresponding $S_0$ structure $B$ is a local maximum (not a true transition state). The transition state $C$ (in reality a shallow biradicaloid intermediate with two transition states) corresponds to the expected allowed asynchronous path. This is almost exactly the picture one would expect from the van der Lugt and Oosterhoff model of the photochemical funnel. However $A$ is not a true minimum! This is illustrated in figure 4b. Here we show the potential surface in the space of a rhomboid distortion. Now the anti-aromatic pericyclic minimum $A$ on the $S_1$ surface becomes a transition state between two conical intersections $E-F$, the upper part of the cone at $E$ is on $S_1$ while the lower part $F$ is on $S_0$. Thus the reaction path on the excited state will not pass via $A$ but rather decay takes place at $E-F$ and the ground state trajectory continues to the biradical region $C$ or cyclobutane $D$. The initial biradical region reached from the rhomboid distortion would be anti but the surface is very flat and the system can rotate about the central C-C bond with almost no barrier.

As a second example let us consider the electrocyclic ring closure of butadiene (a more detailed discussion can be found in ref. [11]). In this example the deviation from the ground state reaction path is extreme. The $S_1$ reaction path is illustrated in Fig. 5.

![Fig. 5 $S_1$ reaction path for the electrocyclic ring closure of butadiene.](image)

The $C_8$ $S_1$ minimum $I$ is disrotated relative to the ground state planar structure but the terminal methylenes do not interact so that this is not the anti-aromatic pericyclic minimum of the van der Lugt Oosterhoff model (see fig. 2 and reference[18]). Rather, the excited state reaction path proceeds over a low ($2 \text{kcal mol}^{-1}$) barrier $TS$ and terminates at a conical intersection $III$. Notice that the reaction path proceeds by rotation about the central C-C bond ($\phi_1$) and a reduction in one of the C-C-C angles ($\omega$). This is in marked contrast with the conventional mechanism which assumes that the C-C-C-C skeleton remains co-planar with simultaneous rotation of the methylene groups. A full survey of the experimental literature can be found in ref. [11]. It is sufficient to remark that the above mechanism is consistent with the fact that fluorescence is not observed in butadiene, and that cis-trans isomerization and bicyclobutane production compete with electrocyclization. The latter (cis-trans isomerization and bicyclobutane formation) follows from fig.3c where it can be seen that several ground state reaction paths may originate from a conical intersection. Indeed, it can be seen that the conical intersection $III$ is already poised for closure to either cyclobutene or bicyclobutane. Thus while in older models, cis-trans isomerization, electrocyclic ring closure and bicyclobutane formation were assumed to proceed via very different reaction paths, we see here that these products can be traced to a single focal point, the conical intersection $III$. The anti-aromatic pericyclic minimum of the van der Lugt Oosterhoff model does not exist!

Now let us consider another textbook example, the di-$\pi$ methane rearrangement (our results and a full summary of the experimental data can be found in reference[10]). The reaction path of the
photochemical di-π methane rearrangement of 1,4 dienes 1 to yield vinylcyclopropanes 4 is usually written as

However, such a mechanism is only formal and in any actual case some or all of the steps may merge into one step and the reaction may become concerted. Thus the central mechanistic question relates to where the excited state reaction path ends and the ground state begins. While 1-4 diradical intermediates have been characterised by theoretical work, there is experimental evidence that appears to suggest that the 1-4 diradical is bypassed and the reaction is concerted. However, a singlet photochemical reaction can only be concerted if it starts on an excited state potential surface and proceeds directly to a ground-state bonding structure via a conical intersection.

On the excited state potential surface, computations reveal the existence of three conical intersection points: a structure a similar to that of the reactant where both π bonds are broken by rotation of the terminal methylenes thus creating a tetraradicaloid, a structure b that corresponds to a rhomboid arrangement of the two ethylenic π systems (ie with a partial 1-3 σ-bond) and a structure c (shown in fig. 6 as C.I.), the lowest energy conical intersection, that occurs in the region of 3. Decay from a (23 kcal mol⁻¹ higher than c) would lead only to cis-trans isomerism or back to starting material. Structure b (31 kcal mol⁻¹ higher than c) has a geometry similar to the conical intersection [2] for the ethylene + ethylene [2+2] cycloaddition and decay would lead to [2+2] cycloaddition products. Structure c (fig 6 C.I.) would be reached via a formal 1,2 vinyl shift and could lead to 3 and 4. However, a search for reaction paths lying in the plane X₁ X₂ (see fig. 2b) yielded only one path that did not lead to disproportion! This reaction path is shown in figure 6. It can be seen that the ground state reaction path leads directly to the 1-3 diradical region of the potential energy surface from which ring closure is immediate.

Fig. 6 $S_0$ reaction path from C.I.

Thus the preferred relaxation pathway from $S_1$ to $S_0$, for the model singlet reaction of 1,4 pentadiene, occurs in the region of the 1-3 diradical thus avoiding formation of the intermediate 2. The diradical 3 is unstable and undergoes a ground state barrierless ring-closure process leading to the final vinylcyclopropane product directly. The important regio- and stereochemical features of the reaction are in agreement with the computed reaction path. In particular the double bond migrates with a rigid sterochemistry.

Conclusions

In this brief summary, the mechanistic implications of conical intersections for organic photochemistry have been discussed. We have limited ourselves to some simple examples so this paper is more in the nature of a tutorial. The main point is that conical intersections form the central mechanistic feature in many organic photochemical reactions. The commonly held view that it is the avoided crossing that occurs at the transition state in thermal reactions that provides the decay point in photochemistry must be discarded.

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