Electronically nonadiabatic thermal reactions of organic molecules

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This *critical review* seeks to bring together organic reactions in which thermal generation of electronic excited states plays an important role. The best known such reactions are those producing chemiluminescent products. However, it appears that there may exist at least as many nonadiabatic reactions in which the excited molecules react before they luminesce. An effort is made to understand the efficiency of excited state production. The crucial roles played by reactive intermediates are highlighted.

Introduction

The thermal reactions of an *n*-atom organic molecule can usually be adequately described in terms of an *N*-dimensional adiabatic potential energy surface (PES), in which a single potential energy can be assigned to every nuclear configuration. The *N* dimensions consist of $3n - 6$ nuclear geometry coordinates and one energy coordinate. The ability to construct such a surface is dependent on the the Born–Oppenheimer approximation, which treats the motions of electrons and nuclei as separable, with the former changing effectively instantaneously in response to the latter.

For photochemical reactions a description in terms of a single PES is obviously insufficient, since the reaction is initiated by promotion of a reactant molecule to an electronic excited state. That fact alone does not invalidate the Born–Oppenheimer approximation, because for many nuclear configurations it may be possible to assign a separate PE surface to each electronic state. Provided the states are well separated in energy, the Born–Oppenheimer approximation may still be quite good for each state in turn. Where the approximation frequently fails is in the vicinity of nuclear configurations at which two or more electronic states become degenerate. These regions provide crucial conduits by which products in their electronic ground states can be formed from reactants in excited states.

This review concerns thermal reactions for which intersection regions between different PE surfaces also play critical roles, but which provide an interesting counterpart to the common photochemical reactions in that they generate products in electronic excited states from reactants in their ground states. Obviously, the products do not stay forever in their excited states. If they return to the ground state by emission of a photon, then the involvement of an excited state is easy to detect as chemiluminescence. However, if fluorescence or phosphorescence of the excited state is not particularly efficient, nonradiative processes, including chemical reactions, might return the excited state to the ground PES. These non-chemiluminescent reactions can be much harder to identify as nonadiabatic events, or put another way, the involvement of electronic excited states in thermal reactions might be more prevalent than one would guess by looking only at the chemiluminescent subset.

The purpose of this review is to examine the literature on thermal nonadiabatic reactions of organic molecules, to look for common physical phenomena that link seemingly disparate reactions, and thereby to assess the likelihood that there could be more thermal reactions involving nonadiabatic events than has been recognized heretofore.

Theoretical analysis of nonadiabatic reactions

Before the 1980s, little of the mechanistic analysis in organic photochemistry involved discussion of conical intersections between potential energy surfaces. However, in recent times their important role has become increasingly recognised and accepted by the organic chemistry community.[1–4] Similarly, for the reactions that form the focus of this review it seems clear

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that conical intersections play crucial roles, and that their existence and characteristics should consequently be discussed.

The regions of intersection between two potential energy surfaces take on characteristics that depend on the spin and spatial symmetries of the electronic states described by each surface. If the states differ in spin or spatial symmetry, then crossing is allowed in $N - 1$ dimensions. If they have identical spin and spatial symmetry (including the common situation in which the nuclear configuration has no symmetry element aside from the identity) then the PE surfaces can cross in $N - 2$ dimensions.[1–4]

The two unique coordinates that lift the degeneracy of two states of identical total symmetry are commonly called the gradient difference and derivative coupling (or nonadiabatic coupling) vectors. When plotted in the subspace of these two coordinates, the intersection takes on the topology of two cones, connected at their points. If the two cones are centred on a more-or-less vertical energy axis, then the upper one forms a "funnel" on the excited-state surface and provides a highly efficient path for returning molecules in their excited states to the ground state. The lower cone is generally bypassed by molecules reacting only on the ground-state adiabatic surface (Fig. 1). Consequently, it may appear that conical intersections are of little direct relevance to thermal reactions. However, that conclusion may be an over simplification. In 1991 Atchity *et al.* provided a more general characterisation of the PESs in the vicinity of an intersection.[5] They pointed out that the axis about which the cones are centred does not have to be parallel to the energy axis. If it becomes sufficiently tilted, then the upper cone need no longer represent a region of unit efficiency for returning the excited-state molecules to the ground state, and the lower surface can have a path for access to the upper surface that is monotonically decreasing in energy (Fig. 2.).[5]

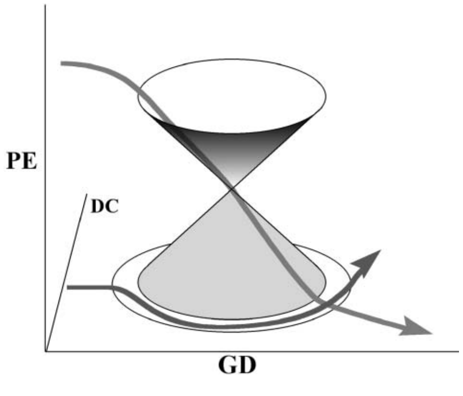


Fig. 1 Schematic representation of a conical intersection. The axis labels are as follows: **PE** = potential energy, **DC** = derivative coupling, **GD** = gradient difference. The two arrows illustrate the contrasting behaviour of reactive trajectories on the upper and lower adiabatic surfaces.

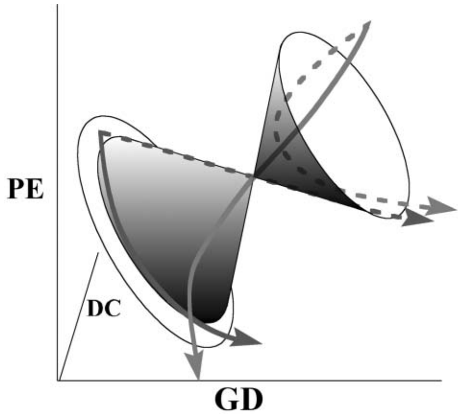
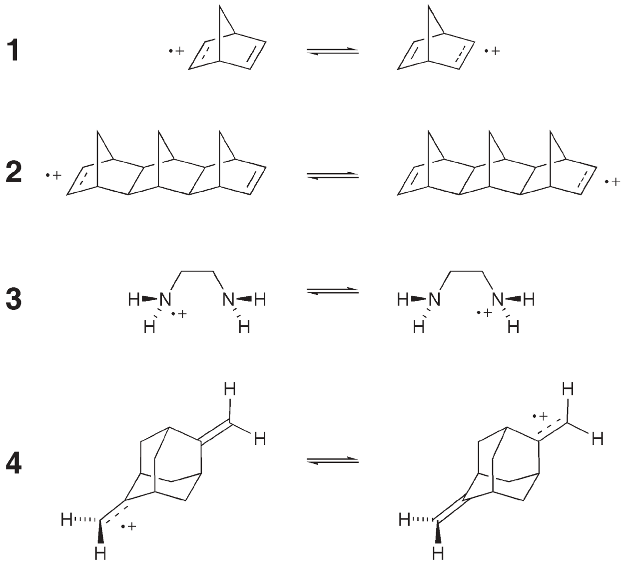


Fig. 2 A sloped conical intersection allows trajectories starting on either surface to end up on the ground state (solid arrows) or the excited state (dashed arrows).

This picture has been further expanded by Blancafort *et al.*, in the context of degenerate, intramolecular hole transfer in radical cations.[6] The equivalent reactant and product in each of these reactions corresponds to a localised radical ion, such as those shown in Scheme 1. The hole-transfer reactions involve symmetrical, delocalised radical ions, which turn out to differ in character for each of the reactions shown. Blancafort *et al.* point out that the differing characters of the reactions can be conveniently classified by considering the relative energies of the two different states corresponding to single occupation of the symmetric or antisymmetric linear combination of donor and acceptor orbitals (^{2}S or ^{2}A, respectively).[6]

Reaction **1** is found to take place on a surface with a sloped conical intersection, such as that stylised in Fig. 2. According to the calculations, the minimum-energy geometries of the ^{2}S and ^{2}A states differ by 19.5 kcal mol^{-1}, with the latter lower in energy. When the symmetry restriction is lifted, the ^{2}A state relaxes to one or the other of the charge-localised minima, which are found to be only 0.1 kcal mol^{-1} lower in energy. The conical intersection between ^{2}S and ^{2}A states occurs at 38.2 kcal mol^{-1} above the reactant. Consequently, this reaction is well described as an adiabatic electron transfer for which the ^{2}A state is the transition state. The conical



Scheme 1 Degenerate hole-transfer reactions considered by Blancafort *et al.*

intersection occurs too far away in energy and geometry to play a significant role.

For reaction **2**, the ^{2}S state is higher in energy than ^{2}A at all geometries. This situation corresponds to a truly avoided crossing, and again signals a strictly adiabatic reaction.

Reaction **3** is found to occur on surfaces that meet in an upright, or "peaked" conical intersection, as illustrated in Fig. 1. The ^{2}S state is now found to have a minimum geometry only 1.1 kcal mol^{-1} above that of ^{2}A, which, in turn, is 3.1 kcal mol^{-1} above the charge-localised minima. The conical intersection occurs at 35.2 kcal mol^{-1} above the minima. Although the intersection occurs too high in energy to be thermally accessed under normal conditions, its presence still has a consequence for the hole-transfer reaction. The lower cone of the conical intersection presents an energetic obstacle to the reaction, which must be circumvented for the hole transfer to occur. Although Fig. 1 illustrates only one pathway for bypassing the obstacle, there are in fact two, corresponding to passage in one direction or the other around the lower cone.[6] These are not equivalent reactions. In fact, for reaction **3**, one reaction involves direct, through-space overlap of the lone pair on one nitrogen with the singly occupied orbital on the other. That reaction has the ^{2}A state as its transition state. The alternative path involves coupling *via* the C–C bond, with the ^{2}S state as the transition state.[6]

Reaction **4** reveals yet another class of PE surface intersections. For this hole transfer, the D_{2d} symmetrical structure is subject to Jahn–Teller distortion, leading to two equivalent D_2 local minima. However, these minima are only 0.12 kcal mol^{-1} below the D_{2d} structure, and the energy difference between electronic states is only 0.47 kcal mol^{-1} at the D_2 geometry. This gap is sufficiently small that the hole transfer can be expected to be essentially purely nonadiabatic. Reaction **4** approximates a situation in which the ^{2}S and ^{2}A states intersect at their respective minimum-energy geometries. Such an intersection creates an $N - 1$ dimensional seam instead of an $N - 2$ dimensional point. In the ideal case of such a reaction, a nonadiabatic reaction would be unavoidable, and in the specific case of reaction **4** it is effectively so.[6]

Since reaction **4** is the only one of the set for which nonadiabatic effects are expected to be significant, one might think that it represents the model of greatest interest for the present review. However, the circumstances leading to nonadiabatic hole transfer in reaction **4** have to do with the particular symmetry properties of the radical ion involved. This is not a commonly encountered situation, and is unlikely to provide a general mechanism for nonadiabatic reactions.

Given that fact, the prospects for generating electronic excited states thermally may look rather bleak. The most general pathway for accessing the upper surface may appear to be *via* a sloped conical intersection, and even in that case it seems improbable that the fraction of reactive trajectories finding their way to the excited state would be large. However, the experimental fact is that there do exist reactions that thermally populate electronic excited states with high efficiency. One purpose of this review will be to see whether it is possible to identify factors that facilitate such events.

One possibility is illustrated in Fig. 3 where a thermal transformation of a reactant with a closed-shell singlet ground state gives a product with an open-shell singlet ground state. If the crossing of closed- and open-shell surfaces occurs after the transition state on the minimum-energy reaction path, then the conical intersection between them will be of the sloped variety that permits access to both electronic states of the product.[5] Furthermore, since real reactions do not proceed at the infinitely slow rate required by the adiabaticity theorem,[7] there maybe insufficient time for the wave function to switch from closed-shell to open-shell character, as the adiabatic reaction would require.

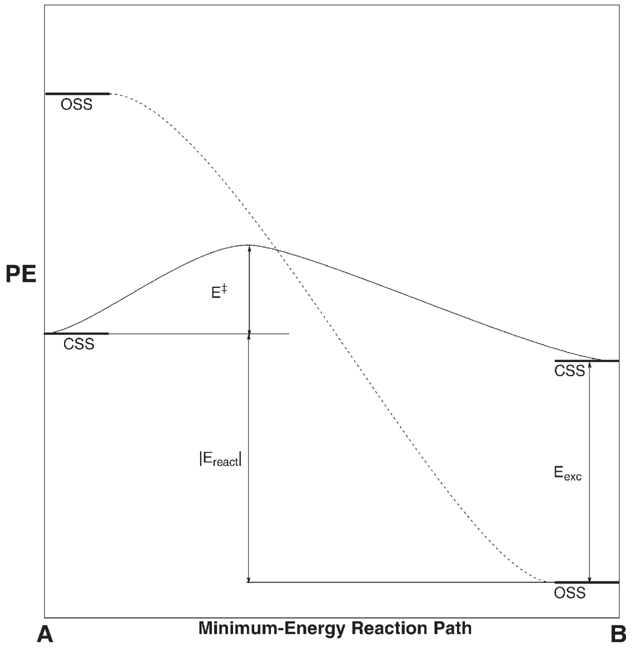


Fig. 3 Schematic reaction profile for the conversion of **A**, which has a closed-shell singlet (CSS) ground state to **B**, which has an open-shell singlet (OSS) ground state. If the crossing of CSS and OSS PE surfaces occurs after the transition state, then **B** may be produced largely in its excited state because of the finite time required to switch the character of the electronic wave function.

Some of the reactions leading to thermal generation of electronic excited states involve changes in total electron spin of the system—generally population of a triplet excited-state product from a singlet ground-state reactant. This spin change occurs by way of spin–orbit coupling, which is here briefly reviewed.[8]

The interaction of an electron's spin magnetic dipole with the magnetic field created by its orbital motion can cause a splitting of otherwise degenerate spin multiplets. More importantly for the present purposes, *changes* in orbital motion of an electron can be coupled with varying degrees of efficiency to *changes* in the spin in ways that conserve overall angular momentum. This spin–orbit coupling is the principal mechanism by which organic molecules undergo changes in total spin, or intersystem crossing (ISC). The coupling serves to mix and split singlet and triplet PE surfaces in the vicinity of their intersection. The larger the spin–orbit coupling, the more facile the ISC. For organic molecules, switches between p-type orbitals oriented along different axes, or π-type orbitals in different planes provide changes in orbital angular momentum that can be coupled to the spin flip required for ISC. Thus, in carbonyl photochemistry, ISC from a $^1(n,\pi^*)$ to a $^3(\pi,\pi^*)$ state tends to occur with much greater efficiency than either $^1(n,\pi^*)$ to $^3(n,\pi^*)$ or $^1(\pi,\pi^*)$ to $^3(\pi,\pi^*)$.

Electronic excited states generated from cyclic peroxides

1,2-Dioxetanes and dioxetanones

Tetramethyl-1,2-dioxetane. 1,2-Dioxetanes form probably the largest class of isolable molecules whose uncatalysed thermal decomposition produces high yields of electronically excited products. The first experimental demonstration of the phenomenon was reported by Kopecky and Mumford, who detected luminescence when 3,3,4-trimethyl-1,2-dioxetane was heated to 60 °C in benzene solution.[9] They assumed that the light was emitted from a singlet excited state, but later studies showed that there was a much higher yield of triplet than singlet excited states produced.[10]

Most of the subsequent research has been carried out on tetramethyl-1,2-dioxetane (TMDO), which also yields primarily triplet, specifically $^3(n,\pi^*)$, excited-state products upon decomposition in solution.[10–23] Despite the extensive research on this molecule, the nature of its decomposition in the gas phase remains much less clear cut. Calorimetric studies and thermochemical estimates have suggested that the transition state for TMDO decomposition is higher in energy than either $S_0 + {}^3(n,\pi^*)$ or $S_0 + {}^1(n,\pi^*)$ products, but it would not be energetically feasible to generate both acetone products in electronic excited states.[11] A reaction involving generation of TMDO by gas-phase reaction of O_2 ($^1\Delta_g$) with tetramethylethylene, led to the conclusion that there was a higher yield of $^1(n,\pi^*)$ than $^3(n,\pi^*)$ acetone products.[21] However, two factors serve to complicate the picture. The first is that the TMDO is produced in a chemically activated state in this experiment, since the transition state (TS) for its formation is estimated to be 26 kcal mol^{-1} higher in enthalpy than that for its decomposition.[21] The second is that the possibility of O_2 quenching of triplet-state intermediates could not be ruled out.[21] Experiments with infrared multiphoton excitation or overtone pumping of TMDO in the gas phase have shown luminescence that corresponds neither to the fluorescence of $^1(n,\pi^*)$ nor the phosphorescence of $^3(n,\pi^*)$ acetone.[24] The authors of this work favoured an explanation involving luminescence from some mixed singlet/triplet excited state.[24] However, later commentators seem to prefer an explanation involving luminescence from an excimer of ground- and excited-state acetone products.[23,25] In any event, until a clearer picture of the gas-phase luminescence of TMDO emerges, there remains the possibility that the apparently high efficiency of formation of $^3(n,\pi^*)$ acetone ($\Phi \sim 0.35$) in solution[26] is dependent in part on some sort of solvent effect. If that were the case, the electronic-structure calculations, which have thus far not included solvent effects, might be intrinsically incapable of fully describing the solution-phase reaction.

The early attempts at mechanistic analysis of TMDO decomposition focused on the question of whether the O–O and C–C bonds broke concertedly or in a stepwise fashion. The concerted reaction would be thermally "forbidden" according to the Woodward–Hoffmann rules, and in one theoretical analysis, that fact was deemed to be responsible for the surface crossings that would allow population of excited state-products.[8] In the alternative view, scission of the O–O bond before the C–C bond was recognised to generate a biradical, which would presumably be formed initially in a singlet state, but for which a triplet ground state could reasonably be expected. If ISC occurred at the biradical stage, then cleavage of the C–C bond could generate one acetone in its ground state and one in the $^3(n,\pi^*)$ excited state.[27]

As seems commonly to be the case with stepwise *vs* concerted debates, the most recent calculations on 1,2-dioxetane decomposition suggest that neither extreme quite captures the mechanism.[23,28] It does appear that O–O bond cleavage is greatly advanced over C–C cleavage in the early stages of the reaction, but the resulting biradical seems to have little or no barrier to fragmentation, and so characterising it as an intermediate in a stepwise reaction would not really be accurate. The proposed course of the reaction is perhaps most easily visualised by adapting the diagrams of orbital occupancies at the biradical geometry, introduced Turro,[8] and then used by Wilsey *et al.*[28] in their calculations on the reaction of the unsubstituted dioxetane (Fig. 4.).

Homolysis of the O–O bond of TMDO can be expected to lead initially to the (σ,σ) biradical in a singlet state. If it were to fragment, then formation of two S_0 acetones might be expected. However, if the $^3(\sigma,\pi)$ surface were to cross the $^1(\sigma,\sigma)$ along the reaction path, then efficient ISC might be expected, since the counterbalancing changes in spin and orbital angular momentum associated with a $^1(\sigma,\sigma)$ to $^3(\sigma,\pi)$ transition might lead one to expect strong spin–orbit coupling at the PES intersection.[8] Once the $^3(\sigma,\pi)$ biradical is formed, it can fragment diabatically to generate S_0 and $^3(n,\pi^*)$ states of acetone.

In the actual CASMP2/CASSCF calculations of Wilsey *et al.* on the fragmentation of the parent 1,2-dioxetane,[28] the picture turned out to be somewhat more complicated than this. First, crossings between (σ,σ) and (π,π) states of the biradical were found, although these are not productive for the overall

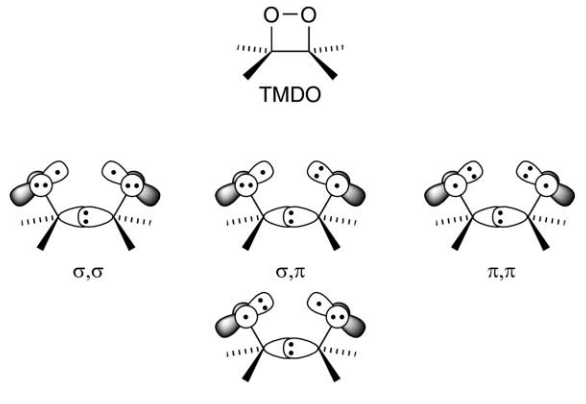
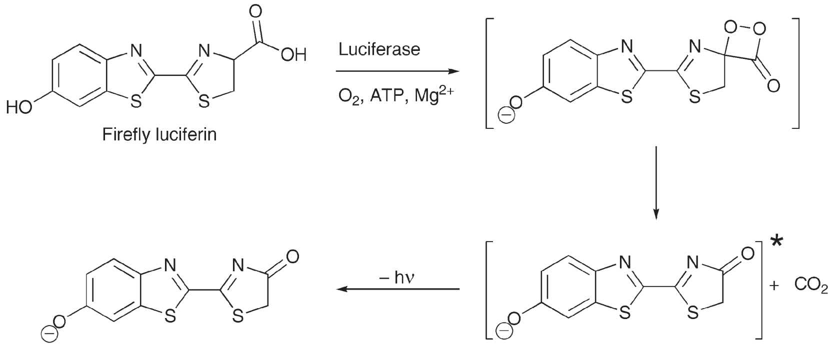


Fig. 4 Tetramethyl-1,2-dioxetane (TMDO) and the principal electronic configurations in the (σ,σ), (σ,π) and (π,π) states of the biradical derived by O–O bond cleavage. Each can exist as a singlet or triplet, and so six different biradical states have to be considered.



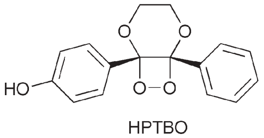
Scheme 2 The accepted mechanism for firefly bioluminescence.

reaction, since the (π,π) state of the biradical would fragment endothermically to give *both* carbonyl products in excited states. Second, a seam of crossing between $^1(\sigma,\sigma)$ and $^3(\sigma,\pi)$ states was found, but it did *not* occur along the minimum-energy reaction path. Instead passage along C–C torsion and O–C–C bending coordinates orthogonal to the minimum-energy path was found to be required before the crossing region was encountered. Whether the lack of $^1(\sigma,\sigma)/^3(\sigma,\pi)$ along the minimum-energy reaction path represents a difference between 1,2-dioxetane itself and TMDO (consistent with such an interpretation is the fact that triplet formaldehyde production from 1,2-dioxetane is much less efficient than triplet acetone formation from TMDO), or whether it is an artifact of the calculations, as later computations have suggested,[23,29] remains to be seen. In any event, where the $^1(\sigma,\sigma)/^3(\sigma,\pi)$ crossing did occur, large spin–orbit couplings ($\sim$60 cm^{-1}) were calculated,[28] as expected from the qualitative picture. As also expected, near-zero couplings were found between $^1(\sigma,\sigma)$ and $^3(\pi,\pi)$ biradical states or between $^1(\pi,\pi)$ and $^3(\pi,\pi)$ states at the intersections of their PE surfaces.

Donor-substituted dioxetanes and dioxetanones

Although the impetus for the synthesis and study of simple dioxetanes was a proposed mechanism for firefly bioluminescence,[30] it turned out that the photophysics of the biological example and its supposed chemical model were different. As discussed above, simple dioxetanes, at least in solution, seem to give higher yields of triplet than singlet excited-state products. However, the luminescence from firefly luciferin (Scheme 2) comes primarily from a singlet excited state.[25]

The connection between firefly bioluminescence and its putative chemical models became stronger when Schaap and Gagnon discovered that deprotonation of the phenol in the dioxetane HPTBO both increased the rate of its decomposition more than a millionfold, and switched the luminescence of the product from principally phosphorescence to entirely fluorescence.[31]



HPTBO

These facts were explained in terms of an electron-transfer mechanism, in which electron donation from the phenoxide to the O–O σ* orbital could both facilitate the bond cleavage and provide a route to singlet excited products. A similar mechanism had previously been proposed for other donor-substituted dioxetanes,[32] and an intermolecular analogue, called chemically initiated electron-exchange luminescence (CIEEL), had been suggested for catalysed decompositions of peroxides (*vide infra*).[33]

As discussed later, the details of the CIEEL mechanism have been subject to some debate. Specifically, the issue is whether a full electron transfer is necessary, or whether partial charge transfer can suffice to promote chemiluminescent peroxide cleavages. Different experimental data seem to support one view or the other.[34,35] The questions, and a possible answer, can be brought into sharper focus for the present intramolecular example by considering the decomposition of a phenoxy-substituted dioxetanone, MPDO, which has recently been studied theoretically by Isobe *et al.* (reaction **5**).[36] Their results can be summarised by reference to orbital occupancy diagrams (Fig. 5) similar to those used for tetramethyl-1,2-dioxetane fragmentation.

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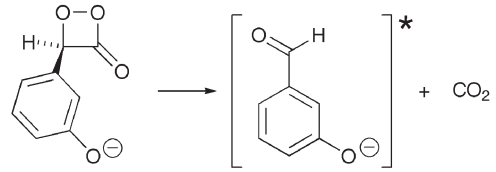


MPDO

The reaction begins with the early stages of dioxetane O–O bond homolysis, just as it does for tetramethyldioxetane. However, in this case, before O–O bond cleavage is complete, the system experiences an avoided crossing with a state derived by electron transfer from the phenoxide substituent to the O–O σ* orbital. The bond scission can consequently be viewed as an adiabatic, dissociative electron transfer. The occurrence of the avoided crossing serves to lower the barrier to bond breaking compared to that for an analogue without the anionic substituent.

The biradical anion intermediate needs a minimum of two electron configurations for proper description. They correspond to localisation of the negative charge on the alkoxide or carboxylate oxygens of the intermediate, and are shown in the

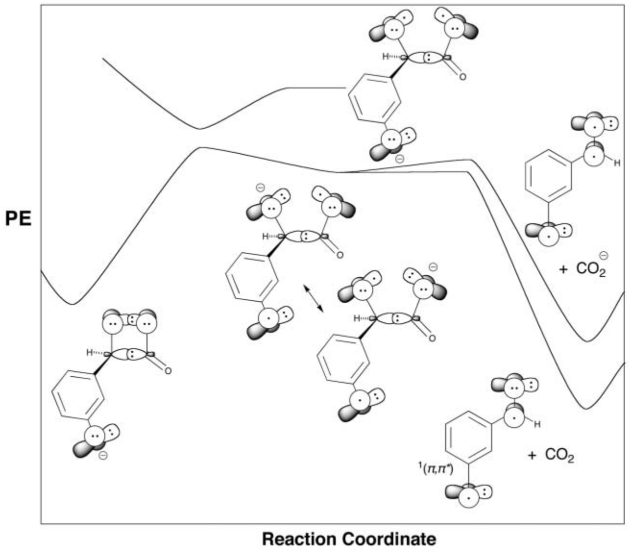


Fig. 5 Schematic PE profile for the decomposition of MPDO. See text for discussion. Note that the change of viewpoint accompanying the C–C bond cleavage may make it appear that there has been a switch of orbital occupancies on the aldehyde oxygen, but in reality there has not.

centre of Fig. 5 with a resonance arrow connecting them. They are the counterparts of the two configurations describing the (σ,π) biradical in Fig. 4. As the C–C bond begins to break in the final step of the reaction, the coupling between the two configurations weakens. Eventually, they become contributing configurations to two different dissociation limits. In one case, neutral CO_2 is formed and the anionic aldehyde product is formed in a $^1(\pi,\pi^*)$ excited state. This pathway consequently requires no back electron transfer to generate the excited state, and so is not strictly a CIEEL mechanism. However, the alternative dissociation limit is, since it gives CO_2^- and an alkoxy-radical substituted benzaldehyde. This pair *would* need to undergo back electron transfer to complete the reaction.

The calculations of Isobe *et al.* favour the direct generation of the aldehyde $^1(\pi,\pi^*)$ state in the gas phase, but make the alternative CIEEL mechanism more competitive when polar solvent effects are included.[36] For both reactions, the crossing with the surface leading to ground-state products (not shown in Fig. 5) apparently occurs relatively late, and so presumably has the character of a sloped conical intersection. It is noteworthy that, in this reaction, formation of the intermediate with a broken O–O bond is apparently adiabatic and that the subsequent C–C bond scission occurs in a way which seems to lead diabatically to the excited-state products. Specifically, in the case of the direct formation of the $^1(\pi,\pi^*)$ state of the aldehyde looks like a natural consequence of C–C bond homolysis, because of the *meta* arrangement of the two ring substituents, which prohibits coupling of the nominally unpaired electrons. Experimentally, it is known that location of the alkoxy substituent in the *meta* rather than the *para* site greatly enhances the yield of excited-state products for a variety of dioxetanes and dioxetanones.[37–39]

Intermolecular donor–acceptor catalysis of peroxide decomposition

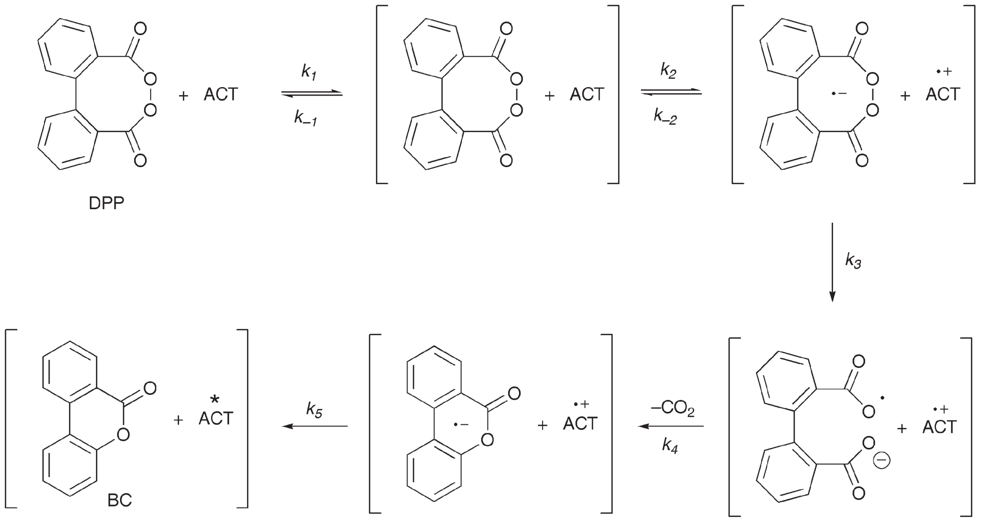
The full details of the CIEEL mechanism, as well as the acronym, came about as a result of studies from Schuster's group on the decomposition of diphenoyl peroxide (DPP).[40] However, as McCapra has pointed out, Linschitz had earlier proposed something very similar to the CIEEL mechanism for the zinc tetraphenylporphyrin catalysed decomposition of tetralin hydroperoxide.[25]

Schuster and coworkers discovered that DPP decomposition was catalysed by a variety of aromatic compounds, or activators (ACT). Those activators capable of catalysis all exhibited fluorescence during the reaction. Furthermore, with one exception, the logarithms of the catalytic rate constants were found to be inversely proportional to the oxidation potentials of the activators. The single exception was pyrene, whose catalytic rate constant would have exceed the diffusion limit if it had adhered to the linear dependence. These facts were nicely consistent with the electron-transfer sequence shown in Scheme 3.[40]

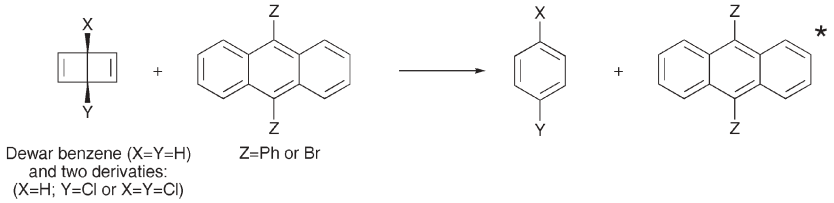
Schuster and coworkers generalised their mechanism to encompass activated chemiluminescence from a variety of compounds, including intermolecular activation for dimethyldioxetanone, and intramolecular activation in luminol and firefly luciferin.[40]

However, a reinvestigation of the DPP decomposition by Catalani and Wilson, as well as an investigation of an apparent CIEEL mechanism in a new dioxetane fragmentation, have led some to question the details of the CIEEL scheme.[34] In particular, it seems that the quantum yield for chemiluminescence, Φ_{CL}, in the DPP reaction is much lower than originally believed. Both it and the dioxetane that Catalani and Wilson studied exhibit Φ_{CL} values of $<10^{-4}$. This fact and a number of others lead these authors to favour a mechanism in which activation occurs only by partial charge transfer between the peroxide and the activator, rather than the full electron transfer proposed in the original CIEEL mechanism.[34]

For the purposes of this review, it is interesting to focus on the very last step of the activated DPP decomposition. This is deemed to occur from a solvent-caged benzocoumarin $^{\bullet -}$/ activator $^{\bullet +}$ radical ion pair in the original CIEEL mechanism, or from a benzocoumarin δ−/activator δ+ charge-transfer complex in the Catalani–Wilson mechanism. Either way, the (partial) charge annihilation is apparently accompanied by much more efficient generation of ground-state than excited-state products. Although the molecules involved in these reactions are too large for calculations that would enable location of the surface conical intersections to be conducted, it seems possible to offer some speculations about the origin of the inefficiency. The reactions discussed so far in which product excited states have been generated thermally with high efficiency seem to have in common crossings with the surface that would lead to ground-state products that occur late in the reaction—*i.e.* when all of the relevant PE surfaces are sloped downward in energy. They also seem to involve reactions for which there is an obvious diabatic connection of an intermediate to the excited-state product, *i.e.* for which formation of the ground state would require a substantial



Scheme 3 The CIEEL mechanism explaining activator catalysis of diphenoyl peroxide (DPP) decarboxylation.



Scheme 4 Stimulation of 9,10-diphenyl- or 9,10-dibromoanthracene fluorescence by thermal ring opening of Dewar benzene or two chlorinated derivatives.

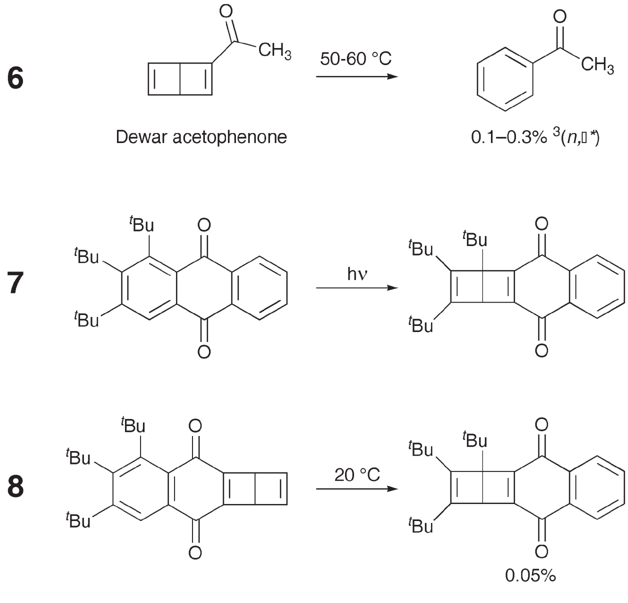
change in the character of the wave function but formation of the excited state would not. In the present example it is not obvious that either of those criteria is satisfied.

Electronic excited states from strained-ring precursors

In 1973 Lechtken and coworkers reported that the ring opening of Dewar benzene or two chlorinated analogues in the presence of 9,10-diphenyl- or 9,10-dibromoanthracene resulted in detectable fluorescence from the polycyclic additives (Scheme 4).[41]

The kinetics of the ring-opening reaction were apparently unaffected by the additives, and so it did not appear that they could be catalysing the reaction. Although the emitted lighted corresponded to fluorescence, Lechtken and coworkers argued that the anthracene derivatives must have been excited by interaction with a benzene *triplet* state, since the S_1 states of the benzene derivatives would not have been thermally accessible during the Dewar-benzene ring openings.

The yield of benzene triplet state from each of the Dewar-benzene ring openings was very low—in every case <0.1%. Nonetheless, this discovery led to the search for other related reactions that might provide excited-state products more efficiently. One such idea, to combine the strained reactant and the fluorescent reporter into one molecule by making a Dewar-anthracene, turned out to yield no detectable emission of any kind.[42] Preparation of a Dewar-acetophenone (Scheme 5, reaction 6) by the Columbia group was modestly more successful.[43] Its ring opening was judged to meet the thermodynamic criteria to provide access to either $^1(n,\pi^*)$ or $^3(n,\pi^*)$ states of acetophenone. However, the total yield of excited-state acetophenone was only 0.1–0.3%, of which ⩾99% was the $^3(n,\pi^*)$ state.



Scheme 5 Variations on the theme of Dewar-benzene ring opening, designed to increase the efficiency of excited-state formation.

More recently, an ingenious technique for detecting low yields of thermally generated excited states was reported by Miki *et al.*[44] They relied on the known photochemical conversion of a tri-*tert*-butyl anthraquinone to one of its two possible Dewar isomers (Scheme 5, reaction 7). They then prepared the other Dewar isomer, thermally ring opened it (Scheme 5, reaction 8), and looked for the photochemical product as an indicator of excited-state formation during the thermal reaction. The strategy was successful, but the efficiency of generation of the excited state was not much greater than that seen with simpler Dewar benzenes. About 0.05% of the characteristic product was detected, which, given the known quantum yield for the photochemical process, translated to about 0.4% yield of the excited state. Because the reaction could not be suppressed with standard triplet quenchers, Miki *et al.* concluded that the isomerisation in reaction 8 occurred *via* a singlet excited state of the anthraquinone intermediate.

The low yield of aromatic $^3(\pi,\pi^*)$ states in these Dewar-benzene ring openings is not surprising, since it is unlikely that there would be large spin–orbit coupling at the accessible regions where S_0 and T_1 surfaces may cross. As described earlier, efficient ISC in organic molecules tends to be associated with transitions between (n,π^*) and (π,π^*) states. For hydrocarbons, including aromatic hydrocarbons, there are no (n,π^*) states, and so ISC tends to be inefficient. In addition, the S_0/T_1 crossing in the ring opening of Dewar benzene has been judged to occur after the transition state, when the system is rapidly dropping in potential energy, and so spends little time in the vicinity of the crossing.[45]

Why Dewar-benzene derivatives that have energetically accessible S_1 product states do not tend to populate those states efficiently (or even at all) is less clear. In order to address the question, calculations of greater sophistication than so far brought to bear on the problem would be necessary. In particular, it would be valuable to search for S_0/S_1 conical intersections and to elucidate their relationship to the minimum-energy reaction path for the ring-opening reaction. The value of such information is illustrated by the ring opening of benzvalene.

In 1976, Turro *et al.* reported the kinetics and thermodynamics of rearrangement of benzvalene to benzene.[46] The reaction turned out to have a slightly higher barrier than the ring opening of Dewar benzene, and was estimated to be about 7.5 kcal mol^{-1} more exothermic. Both of these factors should have made benzvalene a better precursor than Dewar benzene to benzene excited states, if energetics were the only criterion. In reality, no evidence could be found for the generation of any excited-state benzene from benzvalene. The authors ascribed this fact to the differing natures of the two ring opening reactions. Dewar benzene ring opening is a formally "forbidden" reaction according to the Woodward–Hoffmann rules, whereas benzvalene ring opening would be formally allowed. Turro *et al.* argued that only forbidden pericyclic reactions take reacting molecules into regions of their PE surfaces where crossings with other states can be expected.[46] However, modern views of organic reactivity permit a somewhat different analysis. First, while the ring opening of benzvalene is *formally* allowed, the very thermochemistry that Turro *et al.* reported could lead one to doubt that it really is. Surely, since benzvalene ring opening is more exothermic than Dewar benzene ring opening, if the former were allowed but the latter forbidden, the barrier to benzvalene isomerisation should be lower. In reality it is slightly higher. In fact, the most sophisticated calculations on benzvalene ring opening suggest that it occurs *via* the "prefulvene" singlet biradical[47] (Fig. 6). That conclusion is very important for the question of excited-state benzene generation, since the conversion of "prefulvene" to benzene would seem to demand stretching of the C1–C5 bond, which would bring the system very close to a known S_1/S_0 conical intersection for benzene,[48] which occurs at a C1–C5 distance of $\sim$2 Å. The interesting conclusion is thus that the thermal ring opening of benzvalene probably brings the system into the *upper* cone of a conical intersection, and that the very efficient conversion of ground-state benzvalene to ground-state benzene occurs by a reaction through this intersection. If the S_1/S_0 conical intersection occurs earlier along the ring-opening path than any T_1/S_0 crossing, it could also serve to inhibit formation of the triplet excited state of benzene.

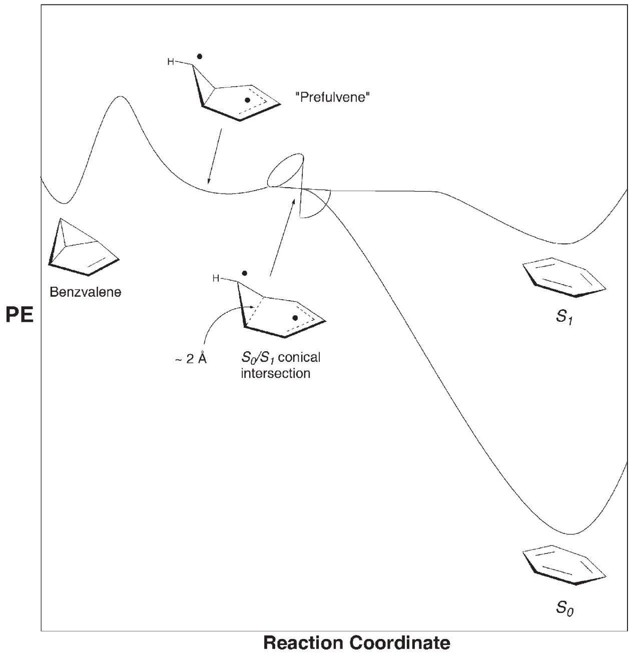


Fig. 6 A schematic PE profile linking the thermal ring opening of benzvalene to a known S_0/S_1 conical intersection of benzene.

The nature of the conical intersection in this reaction is important, particularly to the extent that it differs from that for a similar-looking carbene ring opening discussed below. The calculations of Smith *et al.*[48] characterise the conical intersection as "intermediate" between the "peaked" and "sloped" varieties discussed earlier.[5] Surface-hopping trajectory calculations run in the vicinity of the intersection showed high efficiency for return to S_0 benzene, and very poor interconversion between S_1 benzene and "prefulvene."[48]

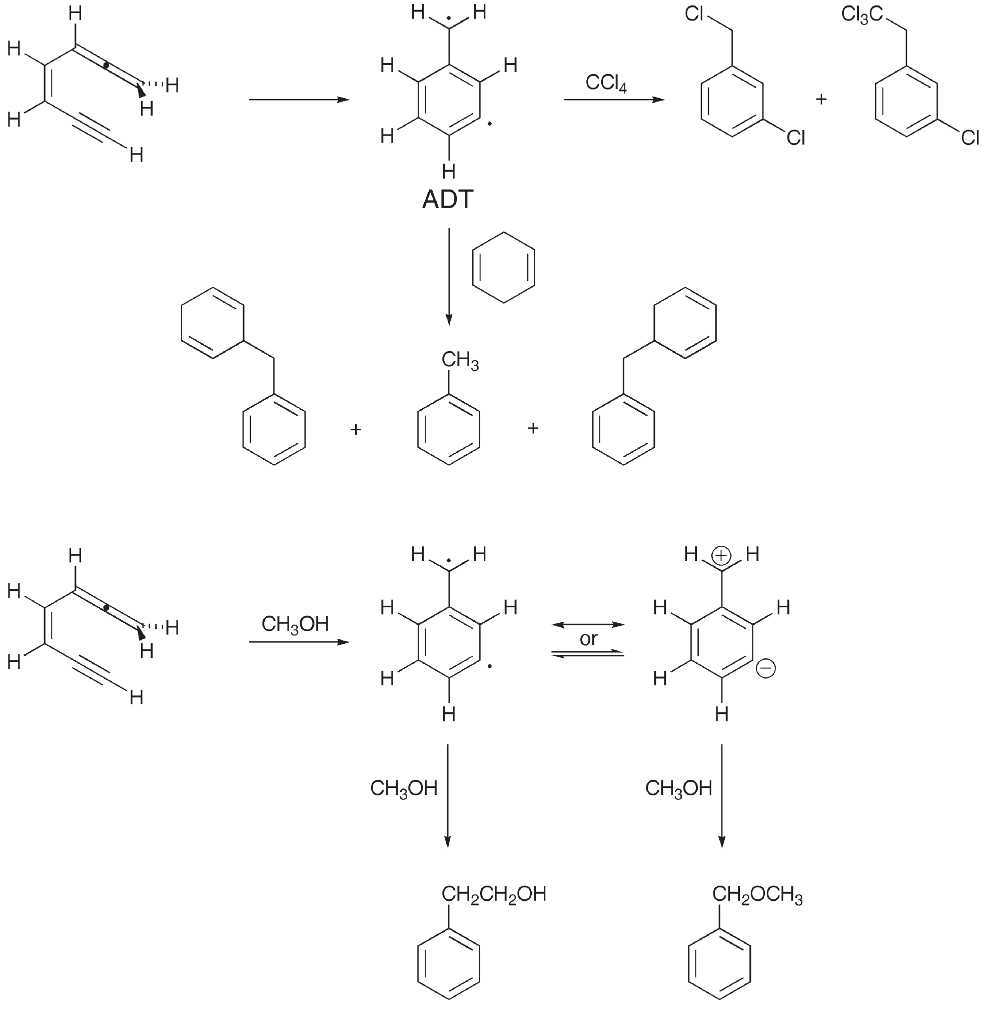
Electronic excited states of reactive intermediates

Organic reactive intermediates differ from isolable molecules in two ways that are important for the present discussion. The first is that they frequently do not have closed-shell singlet ground states. The second is that the energy gaps between electronic states are commonly smaller than those for stable molecules. The consequences of these facts can be seen in Fig. 3. The change in ordering of electronic states between reactant and product makes it possible, at least in principle, to generate an excited state with high efficiency since the character of the wavefunction would have to change drastically in order to take the path to the ground-state product at the conical intersection. The smaller value of E_{exc} when the "product" is a reactive intermediate also makes it easier to satisfy the energy criterion ($|E_{\mathrm{react}}| + E^{\ddagger} \geqslant E_{\mathrm{exc}}$) for population of the excited state. Together, these phenomena suggest that thermal generation of excited states of reactive intermediates could be relatively common.

In the cases where reactive intermediates have triplet ground states, such as for certain carbenes,[49] nitrenes,[50] and biradicals,[51] it has long been known that thermal generation from a singlet-state precursor can lead to an excited electronic state, at least initially. However, that phenomenon has generally been discussed in terms of a need for conservation of total electron spin during the generation step. Implicit in such an analysis would be the expectation that a reactive intermediate with a singlet ground state would therefore not be generated in an excited state if it were prepared thermally from a singlet-state precursor. However, recent examples have shown that such a conclusion need not be correct. They are discussed next in this review.

α,3-Didehydrotoluene

In 1989 Myers *et al.* reported the preparation and rearrangement of (*Z*)-1,2,4-heptatrien-6-yne.[52] The hydrocarbon was designed to be an analogue of the core of the neocarzinostatin chromophore,[53] which is an antitumor antibiotic believed to act by thermal generation of a biradical. The model compound was expected to cyclise to give α,3-didehydrotoluene (ADT), and several of its reactions, such as that with 1,4-cyclohexadiene or CCl_4 (Scheme 6), suggested that it did. However, when heated in methanol, (*Z*)-1,2,4-heptatrien-6-yne gave 2-phenylethanol and benzyl methyl ether in about a 1 : 3 ratio. The former product would be the expected result of H-atom abstraction from the methyl group of the solvent, but the latter looked more like the product expected from an ionic intermediate. After an extensive mechanistic investigation,[54] Myers and coworkers concluded that the ADT biradical was



Scheme 6 Mechanistic proposal from Myers *et al.* for the intermediate(s) formed by thermal cyclisation of (*Z*)-1,2,4-heptatrien-6-yne.

either in rapid equilibrium with, or resonance with a zwitterion (Scheme 6).

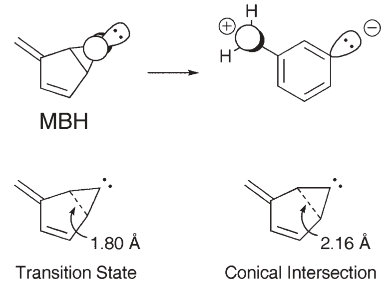
My group was stimulated to work on this problem because we recognised some potential difficulties with the Myers' mechanism. The first was that the biradical/zwitterion resonance ought to be forbidden. In the C_s point group, the biradical representation of ADT corresponds to an A'' electron configuration, whereas the zwitterionic representation is A'.[55] We were also able to show that a single intermediate could not be responsible for the two methanol-derived products, since the ratio of the ether to the alcohol changed linearly with the concentration of added 1,4-cyclohexadiene, up to 0.2 M. This experimental observation would be consistent with the alternative Myers' mechanism, involving equilibration between a biradical and zwitterion, provided that the rate of trapping of the biradical by 1,4-cyclohexadiene was comparable to the rate of interconversion between the intermediates. However, electronic structure calculations did not support this interpretation.

The experimental fact is that the benzyl methyl ether product is favoured over the 2-phenylethanol by about 3 : 1 in the absence of any other trapping agents. If the biradical and zwitterion were in equilibrium, this observation would imply that the transition state for reaction of the zwitterion with methanol would have to be lower in free energy than that for reaction of the biradical with methanol. It also follows that the zwitterion itself could have a standard free energy above the biradical that was no greater than the free energy of activation for reaction of the biradical with methanol. This latter quantity was estimated to be about 9 kcal mol^{-1} by assuming that the barrier to H-atom abstraction by the biradical was the same as that for reaction of phenyl radical with methanol.[56]

In contrast to this experimental constraint on the energy difference between the two intermediates, CASPT2(8,8)//CASSCF(8,8)/6-31G(d) calculations found the zwitterion to be 39 kcal mol^{-1} above the biradical. Although one might expect differential stabilisation of the zwitterion in a polar solvent, B3LYP estimates of the magnitude of that effect could come up with no more than $\sim$10 kcal mol^{-1} reduction in the energy difference between the two—still leaving a gap of $\sim$20 kcal mol^{-1} between the experimental requirements and the theoretical estimate.

Alternative mechanisms, including the involvement of a cyclic allene instead of the zwitterion, reaction of the biradical with *both* C–H and O–H bonds of methanol, and direct involvement of methanol in the cyclization of the reactant, were all considered and experimentally ruled out.[57] The only mechanism that has been found to be consistent with both the calculations and the experimental observations is one in which the cyclisation of (*Z*)-1,2,4-heptatrien-6-yne in methanol preferentially generates the zwitterion as an excited state. This is energetically plausible, because the theoretical estimates and experimental thermochemistry combine to place the zwitterion only $\sim$2 kcal mol^{-1} above the cyclisation transition state in the gas phase.[57] Although it has not yet been possible to do the calculations to prove it, it seems plausible that differential solvation of the zwitterion could bring it down below the cyclisation transition state in a polar medium, such as methanol. Two experimental observations support the proposal of thermal access to the excited state in a sufficiently polar medium. The first is that the effect of 1,4-cyclohexadiene on the ether : alcohol product ratio is to cause a linear increase only up to 0.2 M. At higher concentrations, the plot makes a sharp downward turn.[55] This would be the expected outcome if the decreasing medium polarity raised the relative energy of the zwitterion to a point where it ceased to be thermally accessible. The second observation was made with a derivative of (*Z*)-1,2,4-heptatrien-6-yne having an alcohol trap (the replacement for methanol) chemically tethered to the reactive hydrocarbon. When this molecule was cyclised in a nonpolar solvent (benzene) it gave products ascribable to just the biradical. However, cyclisation methanol again showed the characteristic zwitterion-derived products.[57]

The inability to carry out conical-intersection searches while simulating solvent effects, which hampered a complete theoretical exploration of the (*Z*)-1,2,4-heptatrien-6-yne cyclisation, prompted a search for an alternative precursor that might be able to access the zwitterionic state of α,3-didehydrotoluene even in the gas phase. The carbene MBH (4-methylenebicyclo[3.1.0]hex-2-en-6-ylidene) turned out to be a candidate.[58] CASSCF(8,8)/6-31G(d) and B3LYP/6-31G(d) calculations both showed MBH to have a closed-shell singlet ground state, which would be well described by a configuration having double occupation of a lone-pair orbital in the plane of the three-membered ring and an empty p-like orbital perpendicular to the plane (Scheme 7). If those orbital occupations were to be maintained during the ring opening of MBH to α,3-didehydrotoluene, the ADT would be generated in its zwitterionic excited state. The CASSCF calculations located a conical intersection between open- and closed-shell singlet states that was on or very close to the intrinsic reaction coordinate for the ring opening reaction, and below the transition state for that process.[58] This appears to be a sloped conical intersection, like that in Fig. 2, and so the calculations suggest that both the zwitterionic and biradical states of ADT might be generated during the ring opening of MBH. Although the ratio of the two are difficult to predict without a nonadiabatic dynamics simulation, the qualitative arguments presented so far in this review might suggest that the excited state product would be favoured. Specifically, the conical intersection occurs after the transition state for ring opening, and the formation of the ground-state product would require substantial change in the character of the wave



Scheme 7 The ring opening of carbene MBH to the zwitterionic state of α,3-didehydrotoluene, and the CASSCF results for the transition structure and conical intersection associated with the reaction.

function from that of a closed-shell carbene to an open-shell biradical.

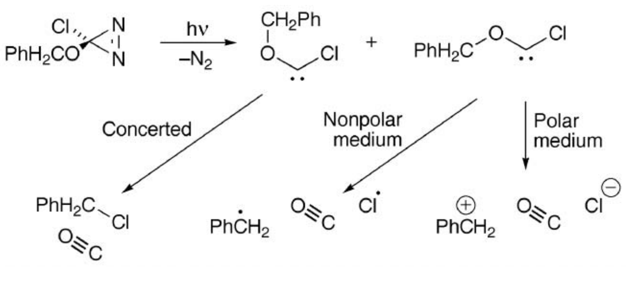
The ring opening of MBH bears an interesting relationship to the ring opening of cyclopropanylidene, studied in detail by Ruedenberg *et al.*[59,60] In that case, too, the closed-shell singlet carbene undergoes a thermal ring-opening reaction, and the PES describing that reaction is intersected by an open-shell singlet surface after the transition state. However, for cyclopropylidene, the lowest energy product is a closed-shell singlet (allene). The open-shell surface connects to the transition state for allene isomerisation, whereas for MBH the open-shell surface connects to the lowest energy product—the biradical state of ADT.

Alkoxychlorocarbene fragmentations

Extensive research from Moss's group at Rutgers University has detailed the interesting fragmentation reactions of alkoxychlorocarbenes.[61] In the gas phase and in nonpolar solvents, these fragmentations are shown to follow competitive concerted and homolytic paths, whereas in polar solvents heterolytic dissociations become possible (Scheme 8).[61]

However, when the study was extended to cyclopropylmethoxychlorocarbene (CPMC), it was discovered that the fragmentation was accompanied by a ring expansion, which known for cyclopropylcarbinyl cation, but not for the corresponding radical.[62] This rearrangement occurred even in nonpolar media for which there had been no prior evidence of heterolytic reactions. Although the full computational exploration of this problem remains to be completed, one working hypothesis for how this reaction could occur is shown schematically in Fig. 7.

The key feature of this proposal is that the larger barrier to ring expansion of the cyclopropylcarbinyl radical causes the radical-pair PES to penetrate the otherwise higher-lying ion-pair surface. In so doing, the system finds a lower-barrier pathway for rearrangement, involving a double surface crossing from radical pair to ion pair and then back again. A very similar mechanism has been proposed for the photodissociation of cyclopropyl iodide.[63]



Scheme 8 Fragmentations of benzyloxychlorocarbene.

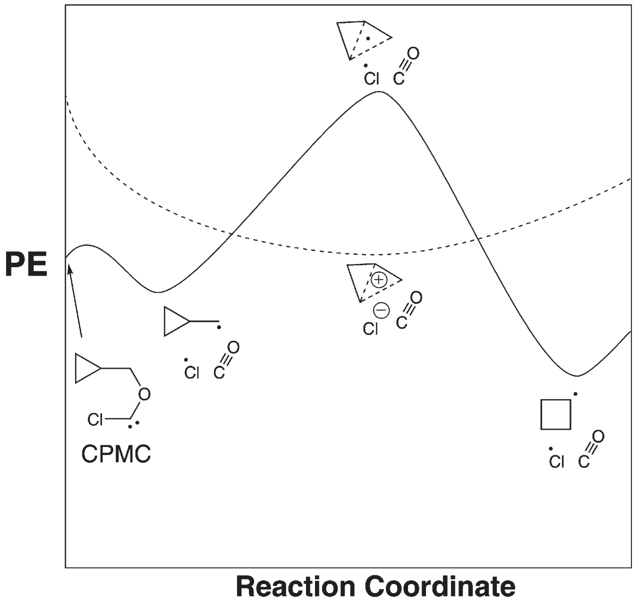


Fig. 7 A schematic profile showing how the observed ring expansion of cyclopropylmethoxychlorocarbene (CPMC) might occur in nonpolar media.

Conclusions

The examples discussed in this review of reactions in which ground-state organic molecules are thermally converted to electronically excited products seem to offer at least the beginnings of some insight into the factors that affect efficiency. Although many details await further more sophisticated calculations, one can at least advance a testable hypothesis. It is that high efficiency in the generation of product excited states in a single-step reaction requires three criteria to be satisfied.

1.) The energy sufficiency condition, $|E_{\text{react}}| + E^{\ddagger} \geqslant E_{\text{exc}}$ (Fig. 3) must obviously be met.

2.) There should be a switch in energy ordering of the electronic states between reactant and product, such that the wave function of the ground state in the reactant is diabatically related to the wave function of the excited state in the product, and *vice versa*.

3.) There should be a sloped conical intersection between ground and excited states occurring after the transition state on the lower adiabatic surface.

The location of the conical intersection along the intrinsic reaction coordinate ensures that the system will spend little time in the intersection region. Since criterion 2 suggests that a substantial change in character of the wavefunction would be necessary to generate the ground-state product, the rapid passage through the intersection region may favour the nonadiabatic reaction.

For single-step organic reactions it is quite unlikely that criterion 2 would be satisfied if both reactant and product were stable, isolable molecules, since the vast majority of stable organic compounds have closed-shell singlet ground states. However, if one or the other of the participants were a reactive intermediate, it is more probable that criterion 2 would be met. The conversion of a ground-state reactive intermediate into an excited-state stable product seems to be what happens in the dioxetane and dioxetanone series of chemiluminescent reactions. This review has attempted to bring to the fore the alternative sequence, in which an excited-state intermediate is generated from a ground-state precursor. Given that many reactive intermediates are just that, *i.e.* reactive, in both ground and excited electronic states, it is entirely possible that they will form products before they have had a chance to luminesce. Thus it can be harder to detect the intermediacy of excited states than it is when excited stable molecules are produced. For that reason, and others discussed in this review, it seems plausible that the involvement of excited states in thermal reactive-intermediate chemistry might be more prevalent than has been recognised to date.

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