

# Avoided Crossings in Excited States Potential Energy Surfaces

A. Devaquet,\* A. Sevin, and B. Bigot

Contribution from the Laboratoire de Chimie Organique Théorique,<sup>1</sup>  
Université P. et M. Curie, 75230 Paris Cedex 05, France. Received April 27, 1977

**Abstract:** The potential energy barriers which govern the kinetic feasibility of photochemical reactions result from avoided crossing between states of similar symmetry. The first type of avoided crossing, as investigated by Salem, is induced in general by the allowed crossing of MOs of different symmetry and intervenes only at the states level. The second, illustrated here in the *ab initio* SCF-CI calculated potential energy surfaces for the *n*- and  $\pi$ -initiated hydrogen abstraction by carbonyl groups, is a direct consequence of avoided crossings between MOs of identical symmetry. The memory of the MOs intended or "natural" correlations shows up—via pseudoavoided crossings of the electronic states—as barriers or wells in the excited states potential energy surfaces.

A factor which is often encountered in determining the kinetic feasibility of a photochemical reaction is whether sufficient activation energy to drive the reaction can be effectively achieved during the lifetime of the potentially reactive excited state, that is, the rate of reaction relative to the rates of excited state deactivation by radiative or radiationless processes is of primary importance. Note immediately the order of magnitude of these activation energies. For an unimolecular or bimolecular reaction to compete, in a singlet state, with fluorescence, its activation energy should be in the 6–9 and 0–3 kcal/mol ranges, respectively. For similar processes to compete, in a triplet state, with phosphorescence these numbers become larger: 14–18 kcal/mol for a unimolecular reaction and 7–11 kcal/mol for a bimolecular event.<sup>2</sup> An important point at issue in the construction of theoretical potential energy surfaces (PES) is then to be able to *predict* the existence of energy barriers, and, in particular, *small* energy barriers.

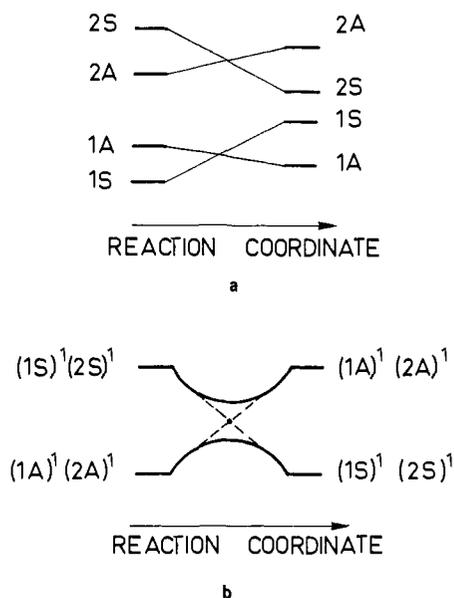
Barriers in the low-lying excited states PES of a reacting system arise from avoided crossings between states of similar symmetry.<sup>3</sup> In other words, these barriers show up as the memory of the intended or "natural" correlations of these states. A typical MO pattern inducing such an avoided crossing is schematized in a two-electron, four-orbital model (Figure 1a). The symmetric (S) or antisymmetric (A) character refers to the behavior of the MOs with respect to a given (unspecified) symmetry operation. The high-lying  $(1S)^1(2S)^1$  state of the reactants continuously decreases in energy and correlates with the low-lying  $(1S)^1(2S)^1$  state of the intermediates (Figure 1b). At the same time the  $(1A)^1(2A)^1$  state of the reactants correlates with the  $(1A)^1(2A)^1$  state of the intermediates (or products). The "natural" crossing of the two curves is symmetry forbidden. The final correlation of the  $(1A)^1(2A)^1$  state of the reactants with the  $(1S)^1(2S)^1$  wave function of the intermediates is characterized by (a) the conservation of the overall electronic symmetry but (b) a simultaneous switch of both electrons from A to S MOs. This analysis accounts for the barriers encountered in the  $^3\pi\pi^*$  photodecomposition of toluene into a hydrogen atom and a benzyl fragment<sup>3b,4</sup> and in the  $^1\pi\pi^*$  elongation of a CH linkage in formaldehyde ( $\alpha$ -cleavage).<sup>5</sup> Let us emphasize that, in this first situation, the avoided crossing occurs between a pair of *states* and that the "natural" correlation of the S and A MOs which induces it is unperturbed by the SCF part of the calculation which treats independently the orthogonal A and S manifolds.

Imagine, however, a pair of MOs of identical symmetry which would tend to intersect each other in the course of a reaction. The resultant mixing will be solved for in the SCF step of the calculations. Barriers or wells in the MOs potential energy curves will eventually appear as the last remnants of the

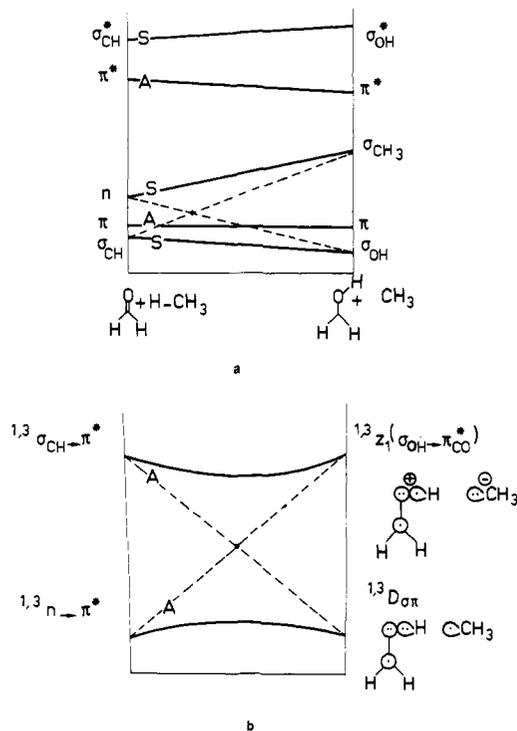
intended but avoided crossing. This in turn will lead to barriers (or wells) in the states PESs. Of course these perturbations will be rather small but their mechanistic importance is not to be underestimated given the limited activation energy an excited state can acquire during its lifetime. In the course of our systematic theoretical study<sup>6</sup> of hydrogen abstraction by ketones we have encountered several examples of this second family of potential energy barriers.

Let us first consider the *n*-initiated hydrogen capture in a simple formaldehyde–methane model. A CH methane bond is broken, an OH counterpart formed. The bonding  $\sigma$  CH MO, destabilized during the elongation of the CH linkage, would finally correlate with the  $sp^3$  hybrid on the methyl moiety ( $\sigma_{CH_3}$ ). At the same time the OH  $\sigma$  bonding orbital is built via the progressive interaction of the oxygen lone pair (*n*) and the 1s hydrogen atomic orbital which is gradually released by the rupture of the CH bond. This means that *n* would naturally be stabilized and correlate with  $\sigma_{OH}$ . The crossing between these two in-plane orbitals is strongly avoided, and, as a result, the final correlation links *n* and  $\sigma_{CH_3}$  on one hand,  $\sigma_{CH}$  and  $\sigma_{OH}$  on the other<sup>3b</sup> (Figure 2a). A state correlation diagram based on these final SCF MOs would directly join the  $^1,^3n\pi^*$  states of the reactants and the  $^1,^3D_{\sigma\pi}$  diradical states<sup>9</sup> of the intermediates. However, such a straightforward reasoning would bypass the consequences of the natural or intended correlations of the MOs, that is, the fact that the  $n\pi^*$  states would wish to reach high-lying  $\sigma_{OH}\rightarrow\pi^*$  excited states of the zwitterionic  $CH_2OH^+ + CH_3^-$  intermediates<sup>9</sup> ( $Z_1$ ) while the  $D_{\sigma\pi}$  states come from a high-lying charge transfer  $\sigma_{CH}\rightarrow\pi^*$  state of the reactants (Figure 2b). There is no avoided crossing *stricto sensu* between these two PESs since the MOs crossing has already been taken into account at the SCF stage of the calculations but the memory of the intended MOs correlations still appears as a small barrier in the  $^1,^3n\pi^*$  states PES (9.2 and 4.6 kcal/mol for the triplet and singlet states, respectively) and a deeper potential well in the corresponding charge-transfer PESs ( $\sim 30$  kcal/mol) (Figure 3).<sup>11</sup> Finally let us remark that the pseudoavoided crossing of the states corresponds physically to the exchange of one electron between MOs of similar symmetry, that is, from *n* to  $\sigma_{CH}$  (or  $\sigma_{OH}$  to  $\sigma_{CH_3}$ ).

The second example we wish to discuss is the  $\pi$ -initiated hydrogen abstraction reaction, again in the simple methane–formaldehyde system in which the captured hydrogen atom ends up at the carbon center of the carbonyl chromophore thus producing methoxy and methyl groups.<sup>12</sup> The calculated MO pattern is represented in Figure 4a. The bonding  $\pi_{CO}$  function which is already localized at the oxygen end of the carbonyl correlates with a pure p orbital of the alkoxy oxygen atom ( $n'_o$ ).<sup>13</sup> The mixing of the three remaining in-plane MOs ( $\sigma_{CH}$ ,

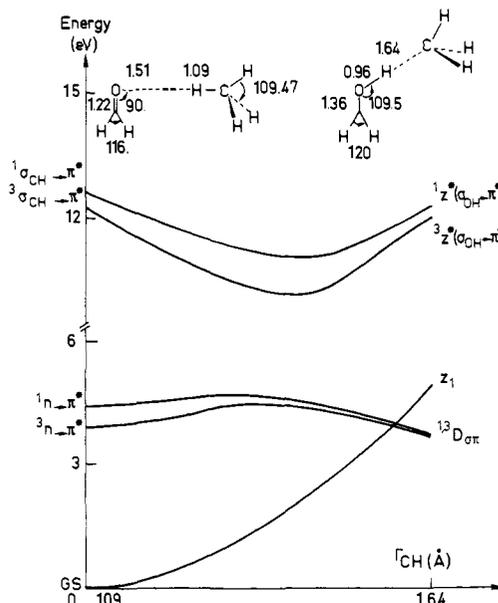


**Figure 1.** (a) Symmetry-allowed crossings of A and S MOs in the four-orbital two-electron model. (b) Symmetry-forbidden crossing of totally symmetric excited wave functions.

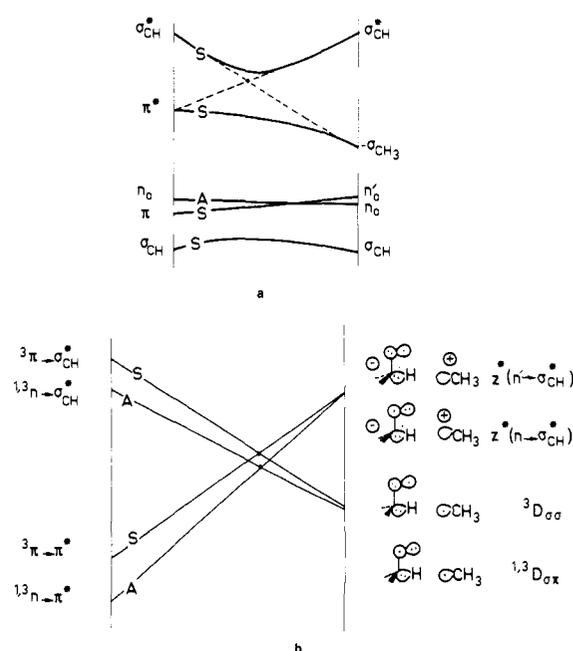


**Figure 2.** (a) Calculated MO correlation diagram in the n-initiated hydrogen abstraction in the formaldehyde-methane system.<sup>10</sup> (b) "Natural" behavior of the nπ\* and σ<sub>CH</sub>π\* excited states of the formaldehyde methane system during the abstraction.<sup>10</sup>

σ\*<sub>CH</sub>, and π\*<sub>CO</sub>) is continuous but involves an intended crossing which is erased at the SCF stage of the calculations. Indeed π\*<sub>CO</sub> which is mainly concentrated on the carbon atom tends to form the antibonding σ\*<sub>CH</sub> orbital and is therefore destabilized. The σ\*<sub>CH</sub> methane MO is stabilized by the elongation of the CH linkage (its antibonding character decreases) and—were it not for the avoided nature of its intersection with π\*<sub>CO</sub>—would correlate with the sp<sup>3</sup>-like orbital of the methyl moiety (σ<sub>CH<sub>3</sub></sub>). Using the final SCF MOs one would predict a straight correlation of the pair of 1,3nπ\* states of the reactants with the 1,3D<sub>σπ</sub> diradical states of the inter-



**Figure 3.** Calculated potential energy curves in the n-initiated hydrogen abstraction in the formaldehyde-methane system (in the starting and final geometries the bond lengths and angles are in ångstroms and degrees, respectively).



**Figure 4.** (a) Calculated MO correlation diagram in the π(C) initiated hydrogen capture in the formaldehyde-methane system.<sup>14</sup> (b) "Natural" behavior of the nπ\* and ππ\* excited states.<sup>14</sup>

mediates on one hand, and of the ππ\* triplet with the D<sub>σσ</sub> triplet diradical on the other. Though the gross behavior of the states would be correctly explained, this analysis overlooks the fact that, for these three states, an additional energy barrier exists which is due to the natural correlations of the antibonding MOs. If one considers this natural evolution it appears that the nπ\* and ππ\* states correlate with (degenerate) excited functions of the zwitterionic intermediates CH<sub>3</sub>O<sup>-</sup> + CH<sub>3</sub><sup>+</sup> (n → σ\*<sub>CH</sub> and n' → σ\*<sub>CH</sub>, respectively). At the same time the D<sub>σπ</sub> and D<sub>σσ</sub> states are linked with high-lying charge-transfer forms of the reactants (namely, n → σ\*<sub>CH</sub> and π → σ\*<sub>CH</sub>, respectively) (see Figure 4b).<sup>14</sup> Of course, the resulting pseudoavoided crossings are strongly prevented by the mixing which has already intervened at the MO-SCF level. Still the system conserves some memory of it in the energy barriers (~20

