

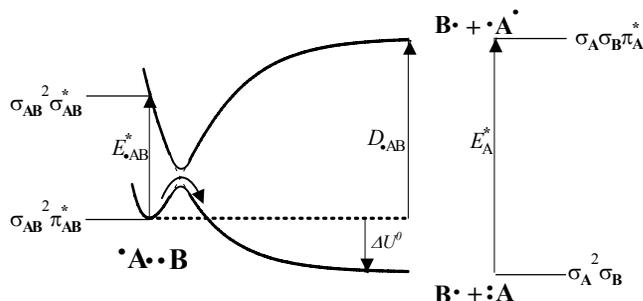
Homolytic Cleavage of Radicals and Ion-Radicals as Intramolecular Dissociative Electron Transfer

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Although electron transfer reactions may lead to chemically stable species, there is a wide variety of instances where injection or removal of one electron into or from a molecule trigger drastic changes in the nuclear framework. Among the changes accompanying electron transfer, particular attention has been devoted to bond cleavage, whether the initial electron transfer to a molecule forms a frangible species that cleaves in a successive step or leads directly to products in a concerted process. In the case of a stepwise mechanism, and starting with close-shell molecules, radicals or ion radicals ($\cdot AB$) are first formed. They are often frangible species that decompose into two fragments. The decomposition may be an heterolytic cleavage, involving a dissociative intramolecular electron transfer ($\cdot A \cdot B \rightarrow A \cdot + \cdot B$), A and B behaving as a donor/acceptor couple.¹ It can also be a homolytic cleavage ($\cdot A \cdot B \rightarrow A \cdot + \cdot B$). If these open-shell systems would behave as closed-shell molecules toward homolytic cleavage, this would be anticipated to be endothermic, following a Morse curve behavior. The process would then be described by a single electronic state and no activation barrier would be expected. Indeed, in a number of cases, it has been found that the homolytic cleavage of cation and anion radicals are endothermic with a small barrier, if any, for the reverse reaction, dissociation being then controlled by the diffusion of the fragments out of the solvent cage.² However as revealed by several experimental examples,⁴⁻⁷ radicals and ion-radicals may undergo exothermic homolytic cleavage with substantial activation barriers. How can one explain the existence of the barrier in these cases?

Considering the fate of the orbitals involved in the bond cleavage and formation process, an orbital correlation diagram is built. A two-state correlation diagram ensues (see below). The homolytic cleavage thus implies that an electron is being transferred from a π^* orbital to a σ^* orbital, and may thus be viewed as a



dissociative intramolecular electron transfer. A two-state semi-classical model is accordingly proposed for explaining the existence of the barrier and estimating its magnitude. It is based on the intersection of the potential energy surfaces characterizing the dissociation of a bonding state, $\cdot A \cdot B \rightarrow \cdot A \cdot + \cdot B$, on the one hand and the approach to bonding distance of a repulsive state, $A \cdot + \cdot B \rightarrow A \cdot : B$, on the other. After inclusion of the bond cleavage and formation as Morse curves in the normal mode analysis, a simple activation driving force relationship is obtained, the two main ingredients of the intrinsic barrier being the triplet excitation energy of the A moiety (E_A^*) and the $\sigma^* \rightarrow \pi^*$ excitation energy in $\cdot AB$ (E_{AB}^*):

$$\Delta G^\ddagger \cong \frac{\lambda_i + \lambda_0}{4} \left(1 + \frac{\Delta G^0}{\lambda_i + \lambda_0} \right)^2 \quad \text{with } \lambda_i = \frac{E_A^* + E_{AB}^*}{2}$$

The model is then tested by quantum chemical calculations, first on a simplified system (methyl vinyl ether anion radical) in order to evaluate the calculation techniques (MP2/6-31G* and B3LYP/6-31G*) and then on a real system (4-cyanophenyl methyl ether anion radical). A comparison of the model predictions with experiment is finally performed using the rate data recently gathered for the cleavage of 4-cyanophenyl alkyl ether anion radicals,⁵ showing satisfactory agreement between theoretical predictions and experimental data.

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