

## Ion / Radical Pair from Dissociative Electron Transfer. Stability as a Function of the Solvent.

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**Abstract.** An ion and a radical are the products of the one-electron dissociative reductive or oxidative cleavage of neutral molecules. There is little doubt that, in the gas phase, substantial attractive interactions between ions and radicals do exist. For example, we found the energy of the interaction between  $\text{CCl}_3$  and  $\text{Cl}^-$  to be of the order of 400 meV by application of quantum chemical method (see figure 1). One expects these interactions to decrease or even to disappear in the liquid phase, particularly in polar solvents. There are however consistent clues that this is not the case, even in solvents as polar as *N,N*-dimethylformamide or acetonitrile, at least when the presence of electron-withdrawing groups induces a positive charge density on the radical atom center that favors its interaction with the counter anion. We recently proposed an extension of the *dissociative electron transfer theory* that integrates the existence of an attractive interaction between the ion and the radical formed upon reductive cleavage. This model predicts rather large kinetic effects (see figure 2).

It appeared on two examples, carbon tetrachloride and 4-cyanobenzyl chloride, that the interaction between the fragments resulting from heterogeneous dissociative reduction (an ion/radical pair) does persist even in very polar solvent. The use of cyclic voltammetric peak potentials as a function of scan rate in four solvents (1,2-dichloroethane, *N,N*-dimethylformamide, ethanol and formamide) form the set of kinetic data on which our exploration has been based. Treatment in the framework of the dissociative electron transfer theory that integrates the existence of an attractive interaction between the ion and the radical formed allowed us to derive the interaction energies. It's variation with the solvent will also be discussed with the help of an attempted correlation with the free energy of solvation of chloride ion.

### References

- 1- C. Costentin, M. Robert, J-M. Savéant, *J. Phys. Chem. A*, **2000**, 104, 7492.
- 2- L. Pause, M. Robert, J-M. Savéant, *J. Am. Chem. Soc.* **2001**, 123, 11908.

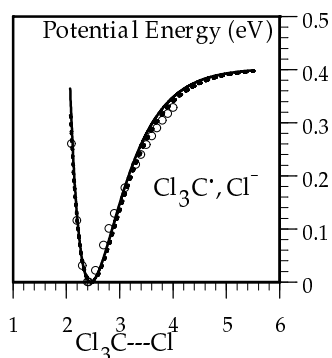


Figure 1. Potential energy profile of  $\text{Cl}_3\text{C}^\bullet, \text{Cl}^-$  in the gas phase. E: MP2 calculation. Solid line: fitting Morse curve.

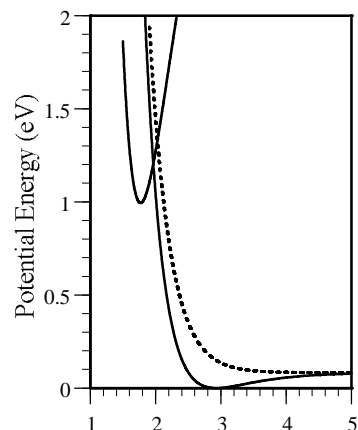


Figure 2. Influence of a small interaction between caged fragments. Morse curves for the reactant, interacting fragments (full line) and separated fragments (dotted line) as a function of the cleaving bond.

Dotted lines:  $\text{RX} \pm e^- \rightleftharpoons \text{R}^\bullet + \text{X}^\mp$

Full lines:  $\text{RX} \pm e^- \rightleftharpoons \text{R}^\bullet, \text{X}^\mp \text{---}$