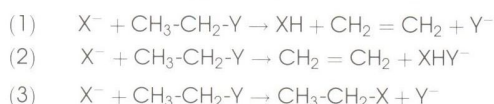


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Solvent Effects on Elementary Chemical Reactions: Competition Between S_N2 and E2 Reactions

Introduction

We have computationally studied anti-E2 elimination (Eq 1), syn-E2 elimination (Eq 2) and S_N2 substitution (Eq 3), which are in principle always in competition for substrates of the type shown below:



Our aim is to arrive at a simple physical model that explains the origin of the reaction barriers in these competing chemical processes. The main point of interest is the computational determination of the still incompletely understood effect of solvation on S_N2 and E2 reactions and, in particular, the competition between the two pathways.

2. Methods and Approach

All calculations were performed with the ADF (1) program package. Previously, we have shown that the ZORA-OLYP/TZ2P approach is suitable for studying our type of model reactions (2). This approach was therefore used to investigate a wide series of model reactions 1, 2 and 3 (see Eq 1-3) with X, Y = F, Cl, Br, I and At in the gas phase and in solution. This involves determining PESes of anti-E2, syn-E2 and S_N2 pathways of the model reaction systems in vacuo and in a model solvent environment using steepest-descent computations. The solvent environment was modeled with the COSMO approach (3).

3. Results and Discussion

In the gas phase, the reactivity of X⁻ is observed in the following order: F⁻ > Cl⁻ > Br⁻ > I⁻ > At⁻. Furthermore, we see a difference of the preference for the competing elimination and substitution reactions. For fluorine the anti-elimination is preferred over substitution in the gas phase, while for Cl, Br, I and At the situation is reversed. I.e. for the latter four atoms, substitution is favored. In all cases is anti-elimination favored over syn-elimination.

In the condensed phase, these patterns change in different ways. For fluorine, substitution now competes more strongly with elimination with a difference in barrier of only 0.4 kcal·mol⁻¹. For the heavier atoms, the condensed phase still significantly favors substitution, but the barrier for elimination is closer to that of substitution. Thus, for X=Y=Br, the difference in barriers reduces from +10.8 kcal·mol⁻¹ (gas-phase) to +8.2 kcal·mol⁻¹ (COSMO), for X=Y=I from +14.3 to +10.0, and for X=Y=At from +16.4 to +11.1 kcal·mol⁻¹. At the same time, all barriers increase significantly, with values for the overall S_N2 barrier (relative to reactants) in the gas phase between -4.2 and +4.0 kcal·mol⁻¹ that turn into values between +16 and +32 kcal·mol⁻¹ in the condensed phase. At the same time, the energy profile of the reactions turns more or less into a unimodal one, with

only very shallow energy minima (of up to ca. 2 kcal·mol⁻¹) observed for reactant and product complexes.

4. Conclusions

In conclusion, solvation slows down all of our model reactions. Furthermore, it shifts the competition in the case of F⁻-induced reactions from E2 into the direction of S_N2. For the heavier halides, S_N2 substitution is anyway preferred over E2 elimination, both in the gas phase and in solution. This follows from our relativistic DFT study of X⁻ + CH₃CH₂Y model reactions (X, Y = F, Cl, Br, I, At) at ZORA-OLYP/TZ2P in which we employed the COSMO model to simulate the effect of solvation in water.

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References

- (1) G. TE VELDE, F.M. BICKELHAUPT, E.J. BAERENDS, S.J.A. VAN GISBERGEN, C. FONSECA GUERRA, J.G. SNIJDERS and T. ZIEGLER, *J. Comput. Chem.*, **22**, 931 (2001).
- (2) A.P. BENTO, M. SOLÀ and F.M. BICKELHAUPT, *J. Chem. Theory Comput.*, **4**, 929 (2008).
- (3) A. KLAMT and G. SCHÜÜRMAN, *J. Chem. Soc. Perkin Transactions*, **2**, 799 (1993).