

ION PAIRS AS INTERMEDIATES IN SUBSTITUTIONS OF BENZILIC SUBSTRATES. A SCRF STUDY INCLUDING SOLVENT EFFECTS.

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ABSTRACT. Self Consistent Reaction Field (SCRF) calculations, including dielectric solvent effects, have been performed to analyze the relative stabilities of the different chemical species found in substitution reactions involving benzilic substrates. The results obtained using the SCRF model, implemented within the SCF - CNDO/2 approach, show that the major part of the solvent stabilization manifests itself during dissociation rather than the formation of ion pairs structures present as intermediate states.

INTRODUCTION

The growing interest in the mechanism of nucleophilic displacement reactions and the structure of the intermediates that occurs along the reaction path, has led several investigators to perform Molecular Orbital studies in these systems. In the case of simple alkyl substrates, evidence in favour of anions stabilized and anion - cation stabilized intermediates (ASI and ACSI, respectively) has been found, rather than the formation of true ion pairs /1/. In benzilic substrates however, the situation seems to be opposite, as it was recently reported /2/. The rationale given for explaining this inversion is based mainly on the delocalization of the charge on the α - carbon of benzyl cation which appears more positive than the corresponding α - carbon in alkyl cation /2/. These conclusions have been derived from MO calculations in gas phase and as a result, their reliability remains constraint to the intrinsic properties of the reacting systems (i. e., inductive effects, charge, localization, etc.).

In solution, the system is expected to be strongly dependent on the properties of the medium since ionic species are involved. The solvent influence may manifest itself in two ways: a) selective stabilization of some species present in the reaction path and b) partial desolvation of at least one side of each reagent during the formation of the ion pairs.

In this work, we present a self-consistent field (SCRF) analysis of the reaction path for the systems shown in Figure 1.

These reactions involving the cases $Y = H, OCH_3$, have been previously analyzed using the MNDO approach without considering solvent effects (2).

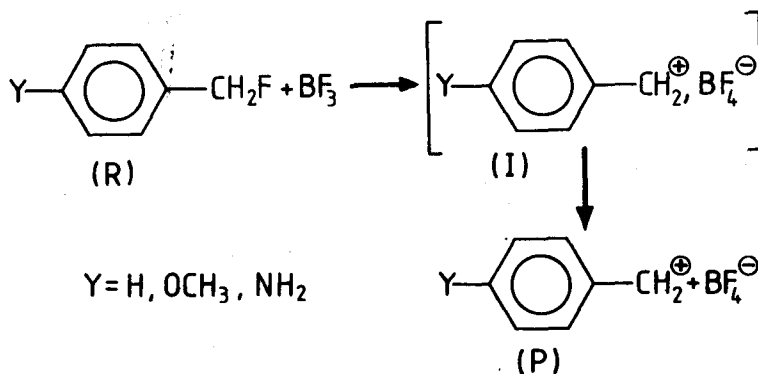


Figure 1. Systems under study

THEORY

Within the continuum approach of solvent effects representation, the total free energy of the solute - solvent system adopts the general form

$$A(\epsilon) = E(1) + \Delta A_s(\epsilon) \quad (1)$$

where ϵ is the bulk dielectric constant of the solvent, $E(1)$, is the total energy of the isolated solute, and $\Delta A_s(\epsilon)$ represents the free energy variations of the solute - solvent system when the solute, in a frozen configuration, is isothermally inserted into the solvent. The diverse models of solvent effects differ mainly by the form in which the quantity $\Delta A_s(\epsilon)$ is calculated. One of the most simple formation for computing ΔA_s , is the well - known generalized Born formula /3 - 5/. In this approach, the solvation energy of any molecular system (ionic or neutral) is build up as a sum of Born - like contributions of each partially charged atomic center. For instance, within a CNDO/2 - like approach, it is expressed as a function of the one particle density matrix as follows:

$$\Delta A(\epsilon, P) = \frac{1}{2} \sum_A Q_A(P) [V_R(\epsilon, P)]_A \quad (2)$$

where $Q_A(P)$ is net atomic charge of atom A, and $V_R(\epsilon, P)_A$ is the reaction field potential acting on the atomic center A of the solute. The basic quantity in this formulation is the reaction field potential $[V_R(\epsilon, P)]_A$ which is obtained from a

set of a polarization (or virtual) charges induced in the dielectric medium. These polarization charges are related to the net atomic charges by the expression

$$Q_A^{\text{pol}}(\epsilon, P) = - \left(1 - \frac{1}{\epsilon}\right) Q_A(P) \quad (3)$$

The RF potential is then derived from $Q_{\text{pol}}^A(\epsilon, P)$, giving /3, 4/

$$[V_R(\epsilon, P)]_A = \sum_B Q_B^{\text{pol}}(P) \gamma_{AB} \quad (4)$$

where, γ_{AB} is the coulomb integral involving the atomic centers A and B. However, in the context of the RF model, these integrals are interpreted as the solute - solvent interaction integrals.

An extension of the GBF has been presented recently /3/. The modification introduced allow the steric hindrance effects upon solvation on each atomic center to be taken into account. The procedure consists in defining an actual polarization charge in the following way.

$$Q_{\text{pol}}^i(P) = - \left(1 - \frac{1}{\epsilon}\right) [1 - f_B] Q_B(P) \quad (5a)$$

and

$$Q_{\text{pol}}^e(\text{pol}) = - \left(1 - \frac{1}{\epsilon}\right) f_B Q_B(P) \quad (5b)$$

This entails

$$\lim_{\epsilon \rightarrow \infty} [Q_{\text{pol}}^i(P) + Q_{\text{pol}}^e(P)] = 0 \quad (6)$$

so that the electroneutrality condition is satisfied for the whole solute.

The reaction field potential at the center A is now a sum of two terms

$$[V_R(\epsilon, P)]_A = [V_R^i(\epsilon, P)]_A + [V_R^e(\epsilon, P)]_A \quad (7)$$

$$\sum_B [Q_{\text{pol}}^i(P)]_B \gamma_{AB}^i + \sum_B [Q_{\text{pol}}^e(P)]_B \gamma_{AB}^e$$

where we have introduced the interaction integrals defined by

$$\gamma_{AB}^i = (1 - f_A) \gamma_{AB} \quad (8a)$$

and

$$\gamma_{AB}^e = f_A \gamma_{AB} \quad (8b)$$

The solute - solvent interaction energy can be written as

$$E_{-s}(\epsilon, P) = \sum_A Q_A(P) [V_R^i(\epsilon, P) + V_R^e(\epsilon, P)]_A \quad (9)$$

and consequently, according to the well - known relationship between $E_{\Sigma-S}$ and ΔA_S , we obtain

$$\Delta A_S(\epsilon, P) = -\frac{1}{2} \left[1 - \frac{1}{\epsilon} \right] \sum_A \sum_B Q_A(P) Q_B(P) [1 - (f_A + f_B - 2f_A f_B)] \gamma_{AB} \quad (10)$$

It follows immediately that Equation (10) contains a first term which is the GBF and a corrective term depending on the neighborhood factors. If we assume that

$$f_B \leq 1, \quad \forall B$$

the correction to GBF has an opposite sign to that of the standard GBF so that it may be interpreted as a desolvation contribution. As expected, this desolvation term disappears when the distance between the atomic centers become larger than overlapping ones (i. e. when $f_B = 0, \forall B$)

A convenient choice for f_B is the following /5/

$$f_B = \frac{1}{2} \sum_{A \neq B} S_{AB} \quad (11)$$

Equation (11) together with Equations (8a) and (8b) give

$$\gamma_{AB}^i \geq \gamma_{AB}^e \quad (12)$$

which implies that $[Q_{pol}^i(P)]_B$ is closer to the B-center than $[Q_{pol}^e(P)]_B$

In other words, $[Q_{pol}^i(P)]_B$ may be considered as an "internal" polarization charge whereas $[Q_{pol}^e(P)]_B$ is an external one. From these considerations, it

follows that the desolvation process appears to be the consequence of a polarization charge transfer from the internal region of the solvent toward the bulk region.

Finally, the effective Fock operator compatible with the solvation free energy given by Equation (10) is obtained from /4/.

$$\Lambda F(\epsilon, P) = \Lambda F(1, P) + \frac{1}{2} \left[\frac{\partial E_{\Sigma-S}}{\partial P} \right] = \Lambda F(1, P) - \Lambda V_R(\epsilon, P) \quad (13)$$

where $F(1, P)$ is the Fock operator of the isolated solute and

$$\Lambda V_R(\epsilon, P) = - \left[\sum_A Z_A \left[\frac{\partial V_R}{\partial P} \right]_A - \text{Tr} P \left[\frac{\partial V_R}{\partial P} \right]_A \right] \quad (14)$$

with $V_R(\epsilon, P)$ given by Equation (7).

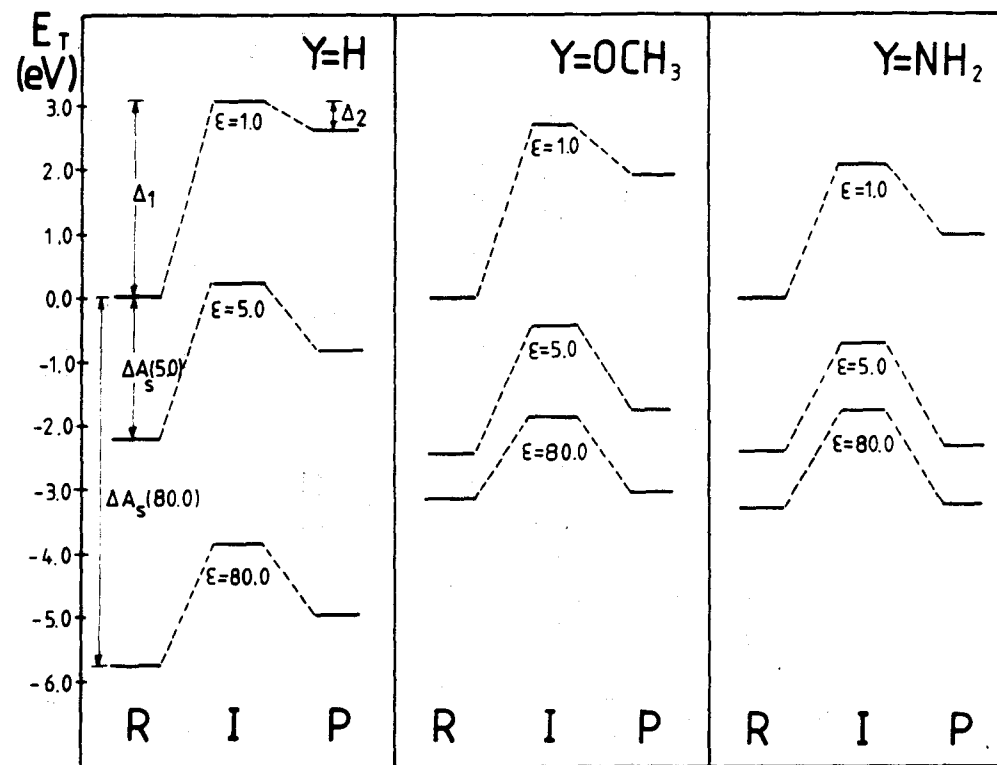


Figure 2. Relative free energies of reagents (R), intermediates (I) and Products (P) involved in reaction 1 for different substituents and different solvents.
 $\Delta_1 = E_T(I) - E_T(R)$; $\Delta_2 = E_T(P) - E_T(I)$ and ΔA_S = solvation free energy.

RESULTS AND DISCUSSION

The geometries of the reagents and products were optimized in the same way as in Ref. /2/ and the geometries of the ion pair were obtained by optimizing only the distance and orientation between the optimized ions. BF_4^- was assumed to be tetrahedral.

The charge distribution obtained, within the SCF - CNDO/2 calculations are qualitatively the same that the one obtained in Ref. /1/. That is, for the ion pair with $Y = \text{H}$, the greatest amount of positive charge is found on the methylene carbon. The ortho and para carbons display a quite similar net charge of about 0.20. For $Y = \text{OCH}_3$, the greatest amount of positive charge is found on the methoxy substituted para - position. This entails that charge distribution in solution follows a similar trend as compared with gas phase calculations. This result confirms the conclusions of Decoret et al. /2/.

The solvent effects may be interpreted from the results summarized in Figure 2. The following observations are relevant:

a) The energy difference, Δ_1 , between the R and I states (i. e., the energy of formation of the ion pair) in vacuum, varies following the order $\text{H} > \text{OCH}_3 > \text{NH}_2$. The same trend is observed in polarizable media with $\epsilon = 80.0$, although with increasing the polarity of the solvent the Δ_1 values decrease as a consequence of the better solvation of the corresponding ion pair compared to the neutral state (R).

b) The energy difference, Δ_2 , between the I and P states (i. e., the dissociation energy of the ion pairs) in vacuum, displays the opposite trend: $\text{NH}_2 > \text{OCH}_3 > \text{H}$. In the presence of the polarizable media with $\epsilon = 5.0$ and $\epsilon = 80.0$, this trend is maintained. However, the following feature is also relevant: the major part of the solvent stabilization manifests itself during the dissociation rather than the formation of the ion pair. This observation is apparent by comparing the Δ_1 and Δ_2 values for a fixed substituent, when ϵ is varied from 1.0 to 80.0. In the present study, this feature appears to be strongly related to the desolvation potential correction introduced in Eq. (1), which is only relevant in the region of the free energy surface corresponding to the formation of the ion pair.

CONCLUDING REMARKS

From the results above described we may conclude that, within the limits of the present approach, the variation of substituent effects are predominant upon formation rather than dissociation of the ion pairs involved as intermediates in these reactions while the solvent effects display the reverse order of importance. These conclusions are consistent with the probable existence of ion pairs as intermediates in these reacting systems and they also confirm the speculation about the solvent effects addressed by Decoret et al. /2/.

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