The Role of Solvent in the Mechanism of Protonation of Benzene and Ethylene

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The hypersurfaces for protonation of benzene and ethylene by H^+ and H_3O^+ species have been studied by means of the MINDO/3 method. Proton solvation reduces the heat of the exothermic reactions, and changes their mechanism. Electrophilic attack is accompanied by desolvation of the proton with this process beginning late in the reaction, the transition state having been passed long before.

In a previous paper [1] the protonation of benzene was studied as a first step in the clarification of the mechanism of electrophilic aromatic substitution. The results then obtained concerned only the process in the gas phase. In the present paper the role of the solvent in the mechanism of protonation of benzene and ethylene is taken into account.

According to both semiempirical [2-6] and *ab initio* methods [7,8] the σ structure of the $C_6H_7^+$ cation is the most stable. For the $C_2H_5^+$ cation *ab initio* methods [8-14] indicate that the σ structure is more stable than the π, the energy difference between both structures being smaller the more extensive the basis set used. When the correlation energy is taken into account [13-17] the π structure clearly appears as the most stable. According to several semiempirical methods [18,19], the π structure is also the most stable. All the above-mentioned calculations show a large proton affinity for benzene as well as for ethylene.

The introduction of the solvent in theoretical calculations may affect the relative stability of the σ and π complexes, the heat of the reaction, and, in a general way, the whole potential surface. Given that the solvent behaves as a nucleophile towards the electrophilic agent, an electrophilic reaction should be accompanied by desolvation of the electrophile. As has already been shown for the redox processes,[20] the charge transfer may be induced by the motion of the solvent molecules and, in general, the charge transfer in ionic species is enhanced by desolvation.[21] Consequently, desolvation may be essential for a correct description of the reaction coordinate in electrophilic attack. On this point Ritchie [22] and Pross [23] have proposed a model based on the desolvation of the electrophile to explain some anomalies in the reactivity–selectivity principle, but these authors disagree on the moment when this desolvation takes place.

To analyse the points mentioned above a discrete model of the solvent must be used. In this work the supermolecule model is adopted. In order to carry out a simplified study of the solvent effect only one molecule of water is considered, as in the solvation of a proton the first molecule of water plays a major role.

CALCULATIONS

Given the impossibility of calculating the potential surface for the majority of reactions of chemical interest, there are two basic approximations which help in overcoming this difficulty: the first consists of reducing the dimensions of the surface, and the second, of locating directly the most interesting points on it. Both approximations are used in the present work.

To reduce the dimension of the potential surface, one or two geometrical parameters are taken as independent variables. For each value of the independent variables all the remaining geometrical parameters of the system are optimized. Because of the number of parameters to optimize, the semiempirical MINDO/3 method [24a] has been chosen in order to maintain the computation time within reasonable limits. The MINDO/3 program [24b] by Dewar, in which the geometrical optimization is carried out by means of the Davidon–Fletcher–Powell algorithm,[25] has been used. For the most interesting points on the energy surface, *ab initio* calculations with a STO-3G basis [26] have been carried out using a modified version of the GAUSSIAN 70 series of programs.[27]

The direct location of the stationary points on the potential surface has been made by using the method proposed by McIver and Komornicki [28] by means of the SIGMA program † which minimizes the gradient norm. In a later step, using the FORCE program † which diagonalizes the force constant matrix, the nature of these points is determined.

RESULTS AND DISCUSSION

We present first the results for ethylene, and secondly for benzene.

For the $C_2H_5^+$ cation the MINDO/3 method, optimizing all the geometric parameters, shows that the π complex is 32.63 kJ mol^{-1} more stable than the σ complex. This result is in good agreement with the *ab initio* results in which the correlation energy has been taken into account.[13-19] Upon solvating the proton with a molecule of water, the π complex is the most stable. In this complex the distance between the proton and the oxygen atom is 2.87 Å; this distance has a value of 0.96 Å in the H_3O^+ species. This shows that the electrophilic attack of the solvated proton on ethylene is accompanied by desolvation.

As the π complex is the most stable, we only calculate the potential surface for the formation of this complex. In Figures 1 and 2a, we present the curves of the poten-

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† The SIGMA and FORCE programs were written originally by Dr. A. Komornicki, and implemented by S. Olivella, and R. Caballoll.

tial energy for the formation of the π complexes of $C_2H_5^+$ and $C_2H_5H_2O^+$. These energy profiles have been obtained by optimizing, for every value of the proton–carbon distance taken as an independent variable, all the remaining geometrical parameters. The restriction that the proton remains over the middle point of the C–C bond is imposed. In the gas-phase protonation the potential energy curve decreases regularly from the reactants to the final product. It has a heat of reaction of -660.23 kJ mol^{-1} in good agreement with the experimental value of -669.44 kJ mol^{-1}.[29] A parallel may be observed between the charge transfer from ethylene to the proton, measured as the atomic orbital population on the proton, and the energy stabilization of the system throughout the whole process. When the attacking species is the proton solvated with a molecule of water (Figure 2a), an intermediate for the proton–carbon distance of 5.5 Å is formed initially, and is followed by a transition state at a proton–carbon distance of 2.7 Å with a small potential barrier of 4.60 kJ mol^{-1}. The heat of the reaction is -85.77 kJ mol^{-1}. The diminution of the exothermic effect of ethylene protonation on going from the gas phase to aqueous solution is clearly reflected in these results in spite of the simplicity of the model adopted. It may be observed, as well, that the charge transfer from ethylene to the solvated proton, measured as the increment of atomic orbital populations on the H_3O^+ species, takes place in a very advanced phase of the process. In Figure 2b the potential surface for the formation of the π complex of $C_2H_5H_2O^+$ is shown. The proton–carbon and proton–oxygen distances are taken as independent variables. Along the reaction path on this surface it is apparent that the proton–oxygen distance varies appreciably only for a value of 1.6 Å for the proton–carbon distance. So, desolvation takes place after the transition state, in the last phase of the process when the charge transfer is made. This theoretical result supports Ritchie's model.[22]

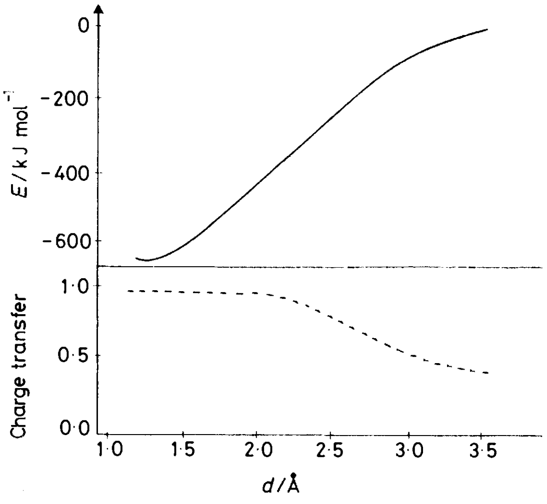

FIGURE 1 Energy profile and charge transfer for the formation of the π complex of $C_2H_5^+$. The proton–carbon distance is taken as an independent variable

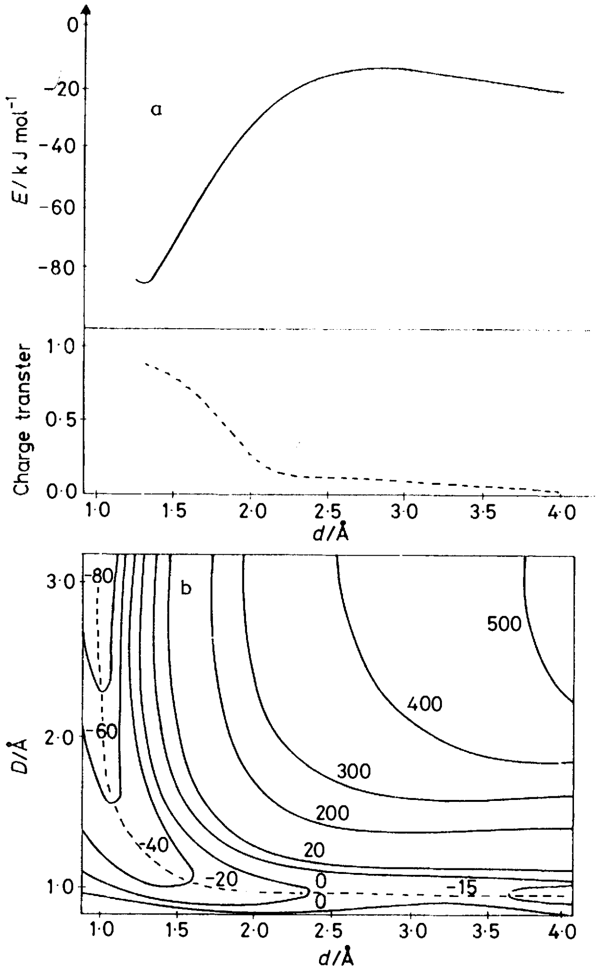

FIGURE 2 Formation of the π complex of $C_2H_5H_2O^+$. a, Energy profile and charge transfer as a function of the proton–carbon distance. b, Potential surface as a function of the proton–carbon, *d*, and proton–oxygen, *D*, distances

Let us now analyse the results for benzene. In the $C_6H_7^+$ cation the σ complex is 32.10 kJ mol^{-1} more stable than the π complex according to the MINDO/3 method.[1] In the $C_6H_7H_2O^+$ species the σ complex is still 31.3 kJ mol^{-1} more stable than the π complex. This result is in good agreement with the value obtained by Olah in superacid solution.[30] The proton–oxygen distance is 3.04 Å in the σ complex, and 2.68 Å in the π complex. As before, this gives evidence that benzene protonation is accompanied by proton desolvation. Because in the formation of the σ complex of $C_6H_7^+$ there are two different channels, one passing through the π complex, and the other going directly to the σ complex,[1] the surface for the formation of both σ and π complexes has been studied. In Figure 3 the potential energy curve for the formation of the σ complex of the $C_6H_7^+$ cation is presented. The proton–carbon distance, taken as an independent variable, was gradually increased from the σ complex (1.11 Å), allowing all the remaining geometrical parameters to be optimized. From a value of 1.5 Å the proton shifts to positions closer to one of the neighbouring carbon atoms preventing a complete profile from being obtained. The heat of the reaction is -696.9 kJ mol^{-1},

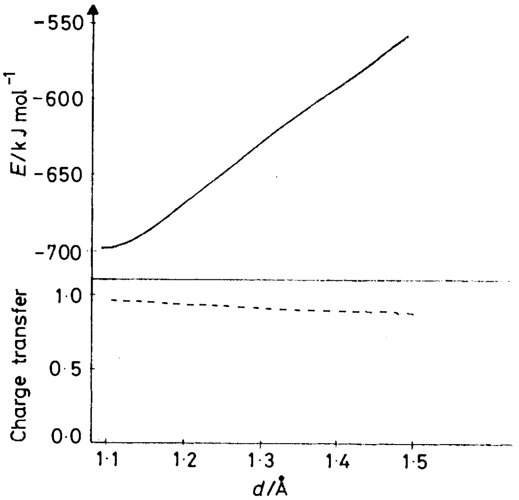

FIGURE 3 Energy profile and charge transfer for the formation of the σ complex of $C_6H_7^+$. The proton–carbon distance is taken as an independent variable

in good agreement with the experimental value, —744.8 kJ mol^{-1}.[31]

With the solvated proton (Figure 4a) the heat of the reaction is only —117.15 kJ mol^{-1}, and once again a diminution of the proton affinity on going from the gas phase to solution appears. As a result, intermediates and transition states occur along the reaction path. The first intermediate occurs at a proton–carbon distance of *ca.* 3.0 Å, followed by a transition state at *ca.* 2.65 Å. A second intermediate occurs at 2.4 Å followed by a transition state at 2.1 Å before the arrival at the final product. The second intermediate is accompanied by an increase in the charge transfer from benzene to the solvated proton, although the charge transfer becomes large only in the last phase of the process. In Figure 4b the potential surface for the formation of the σ complex of $C_6H_7H_2O^+$ is shown as a function of the proton–carbon and proton–oxygen distances taken as independent variables. In the reaction path on this surface the proton–oxygen distance does not change appreciably until a proton–carbon distance of 1.5 Å is reached. The proton-desolvation process takes place in the last phase of the reaction long after the last transition state, and parallel with the charge transfer. This result supports Ritchie's model.[22] Nevertheless, it must be pointed out that some of the isoenergetic lines in Figure 4b have been obtained by extrapolation in some areas. For proton–carbon distances of *ca.* 1.8 Å, and proton–oxygen distances above 2.4 Å, the proton, as in the gas phase, shifts to the neighbouring carbon atoms. For proton–carbon distances above 2.7 Å and proton–oxygen distances above 1.8 Å, lower energy structures were obtained due to the formation of the $C_6H_5^+$ cation and a H_2 molecule solvated by the water molecule.

The intermediate occurring at 2.4 Å, has these characteristics: the carbon–hydrogen distance has lengthened and the formation of the H_2 molecule is beginning. To analyse this intermediate and the subsequent transition state, we have used the SIGMA program. The stationary point located on the surface from the intermediate corresponds to a conformation in which the attacked carbon, the hydrogen atom linked to it, the attacking proton, and the oxygen atom of the water molecule are linear. For this structure the FORCE program renders only one negative eigenvalue in the force constant matrix. Nevertheless, this negative eigenvalue is very small, of the order of 10^{-4}, and the corresponding normal co-ordinate is a vibration of the water molecule. In the conformation obtained by means of the SIGMA program from the transition state at 2.1 Å the linear structure of the intermediate has been lost. The FORCE program shows this conformation to be a true transition state as the diagonalized force constant matrix presents only one negative eigenvalue. The corresponding eigenvector which defines the reaction co-ordinate corresponds to a shift of the solvated proton to a π type position. This transition state is 6.69 kJ mol^{-1} less stable than the previous structure confirming it as an intermediate. In the energy profile (Figure 4a) sketched by recalculating the MINDO/3 structures of the reagents, the products, the intermediate at 3.0 Å, and

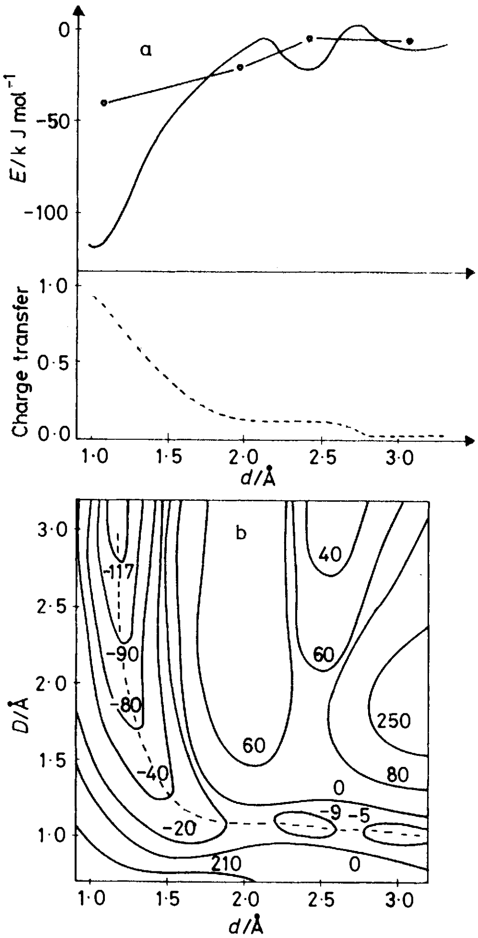

FIGURE 4 Formation of the σ complex of $C_6H_7H_2O^+$. a, Energy profile and charge transfer as a function of the proton–carbon distance. The circles represent the structures recalculated with STO-3G. b, Potential surface as a function of the proton–carbon, *d*, and proton–oxygen, *D*, distances

the two stationary points, located with the SIGMA program, with the *ab initio* method at a STO-3G level, the second intermediate has disappeared, putting into question the physical meaning of such a structure.

The formation of the π complex of the $C_6H_7^+$ cation (Figure 5) has a potential energy curve completely analogous to that for the formation of the π complex of the $C_2H_5^+$ cation. In the same way, the curve for the formation of the π complex of the $C_6H_7H_2O^+$ species (Figure 6a) is analogous to that for ethylene: an intermediate occurs initially followed by a transition state at a proton–carbon distance of 2.7 Å. Figure 6b shows the reaction path on the potential surface for the formation of the π complex of the $C_6H_7H_2O^+$ cation. The proton–carbon and the proton–oxygen distances have been taken as independent variables. As can be seen in Figure 6b, desolvation of the proton takes place, once more, at the end of the reaction, from a proton–carbon distance of 1.7 Å, supporting Ritchie's model.[22] Comparing Figure 6a with Figure 4a it can be observed that the formation of the σ complex is possible both directly or by passing through a π complex. The energy of the first transition state on the σ profile, for a value of the proton–carbon distance of 2.6 Å, is the same as the energy of the transition state at 2.7 Å on the π profile. From this moment until the proton–carbon distance reaches 2.1 Å the σ path is favoured. From 2.1 to 1.3 Å, when the π complex occurs, the reaction path on the π profile is favoured. At 1.3 Å the π complex is 18.83 kJ mol^{-1} more stable than the corresponding point of the reaction path on the σ surface. Consequently, the previous formation of the π complex appears as an alternative pathway, the last transition state at 2.1 Å being a possible connection between the σ and π surfaces.

It has been reported [32] that the MINDO/3 method has some deficiencies in dealing with some neutral structures containing heavy atoms linked by hydrogen bonds, leading to incorrect interatomic distances and interaction energies. In the present work, the MINDO/3 structures for the charged species are essentially correct. Nevertheless, at the end of the reaction when charge transfer becomes appreciable the MINDO/3 method provides structures where desolvation is overemphasized.

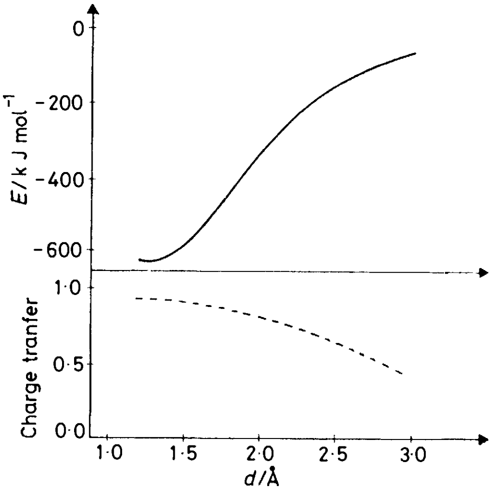

FIGURE 5 Energy profile and charge transfer for the formation of the π complex of $C_6H_7^+$. The proton–carbon distance is taken as an independent variable

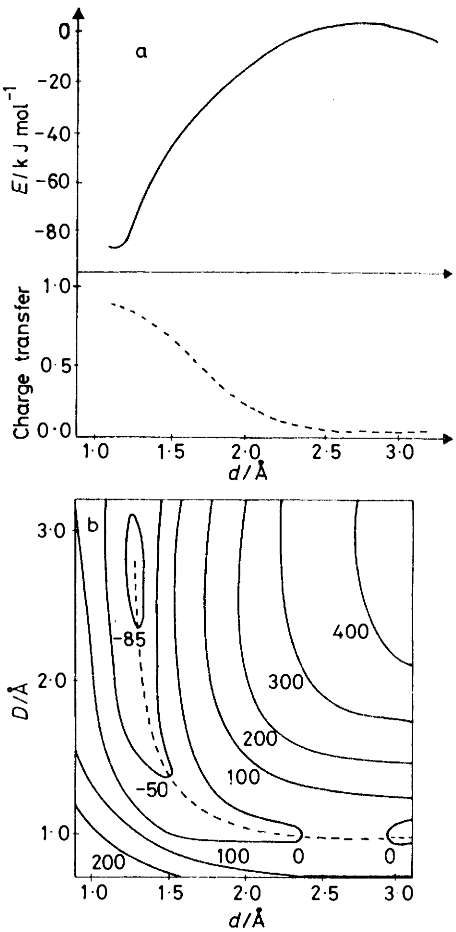

FIGURE 6 Formation of the π complex of $C_6H_7H_2O^+$. a, Energy profile and charge transfer as a function of the proton–carbon distance. b, Potential surface as a function of the proton–carbon, *d*, and proton–oxygen, *D*, distances

In spite of these limitations of the calculation method, it seems that this study permits the following conclusions.

The solvent effect reduces the heat of exothermic reactions because of the dissimilar charge delocalization in products and reagents.

Intermediates and transition states occur only by taking into account solvation, electrophilic attack then being a multi-step reaction.

Electrophilic attack is accompanied by desolvation of the proton, with this process beginning late in the reaction, the transition state having been passed long before. This fact may be considered as theoretical support of Ritchie's hypothesis explaining the constant selectivity relationship which occurs in some electrophilic substitutions. Nevertheless, it must be pointed out that the proton is a very special electrophilic reagent and is very strongly bonded to the first water molecule. In order to generalize these results the study of other electrophilic agents is required.

Water acts as a nucleophile diminishing the electron affinity of the proton and retarding the charge transfer process. Charge transfer to the H_3O^+ ion is enhanced by desolvation of the proton, and, on the other hand, desolvation is produced by charge transfer as the LUMO of the H_3O^+ is antibonding between H^+ and H_2O. For cationic electrophiles, then, desolvation will play an essential role in the reaction co-ordinate.

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