# Effects of Solvation on the Pairing of Electrons in a Series of Simple Molecules and in the Menshutkin Reaction

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The effects of solvation on the pairing of electrons in molecules have been analyzed in a series of molecules and in the Menshutkin reaction between ammonia and methyl chloride. Solvation in water and chloroform has been modeled by means of the polarizable continuum model. A comparative analysis of the electron-pair structure of all the molecules studied has been carried out in the framework of the atoms in molecules theory. In particular, atomic populations and localization and delocalization indices have been used for describing the electron-pair characteristics of all the molecules. In general, this analysis shows that solute-solvent interactions modify the electron-pair distribution of the solute increasing the polarization of the molecular bonds. The electron-pair characteristics of the different stationary points found in the Menshutkin reaction have been also analyzed in detail. The evolution of electron pairing along the reaction path has also been followed in vacuo and in water. Comparison of the results obtained reveal that the main difference between the reaction in gas phase and in water is the structural and electronic advance of the transition state towards the reactant side. Finally, the Menshutkin reaction with explicit representation of the solvent molecules has been studied to discuss the relevance of charge-transfer and specific interactions between the solvent and the solute.

## Introduction

Solvent effects in atoms and molecules are of great importance in studies of molecular structure and chemical reactivity. In particular, the solvent can modify extensively the potential energy surface (PES) of many reactions, especially when charged or polar species are involved. With respect to a system in gas phase, the presence of solvent generally leads to an energetic stabilization of the solute, together with changes in the molecular geometry and a redistribution of the electron density. In principle, in ab initio calculations, one could introduce explicitly the solvent molecules, treating both solute and solvent at the same level of theory. In practice, this approach is generally not feasible from a computational point of view, and one has to model the effect of the solvent on the solute. The most usual choice is to treat the solvent as a continuum dielectric medium, which induces a certain polarization in the solute wave function. Different solvents can be simulated by using different values for the permittivity of the dielectric medium ($\epsilon$). The first practical implementation of the polarizable continuum model (PCM) was that of Miertuš, Scrocco, and Tomasi (MST).[1] Further work in this area has led to the development of several approaches for introducing solvent effects in ab initio or semiempirical calculations.[3−5]

In PCM methods, the solute is located into a cavity surrounded by a continuum dielectric medium which models the solvent. The solvent reacts against the solute charge by generating a reaction field, which is usually added as a perturbation, $\hat{V}$, to the solute Hamiltonian, $\hat{H}_0$

$$(\hat{H}_0 + \hat{V})\Phi = E\Phi \qquad (1)$$

Because of the dependence between the perturbation operator and the wave function, eq 1 above must be solved iteratively. Thus, this particular methodology is usually referred to as self-consistent reaction field (SCRF). Nevertheless, eq 1 can also be solved by a matrix-inversion approach,[2] which gives equivalent results to the SCRF method.

In the last years, many theoretical studies have been devoted to analyzing the effects of several solvents in chemical reactions.[3−5] These analyses have been focused mainly on the changes due to solvent−solute interactions on molecular energies, geometries, and charges. In contrast, few studies have aimed at analyzing solvent effects on the electron charge distributions of atoms and molecules. In these studies, it has been found that inclusion of solvent effects leads to significant changes in first-order electron density distributions[6,7] and on its radial moments.[8] However, to our knowledge, no investigation has been carried out yet to analyze solvent effects on second-order density distributions.

The atoms in molecules (AIM) theory[9] provides a solid theoretical framework for analyzing molecular electron density distributions. One of the basic points in the AIM theory is the possibility of dividing a molecule into its constituent atoms using only the one-electron density distribution. Thus, an atom in a molecule is defined as a region in space (an atomic basin) bounded by zero-flux surfaces in the one-electron density, $\rho(\mathbf{r})$, or by infinity. Atomic properties, such as atomic electron population, atomic energy, etc., are obtained by integration through atomic basins. Furthermore, by means of the two-electron density function, $\Gamma(\mathbf{r}_1,\mathbf{r}_2)$, one can also determine how the electrons in a molecule are localized into individual atoms or delocalized between pairs of atoms.[10] The instantaneous exchange and correlation effects taking place between the

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electrons in a molecule can be described by means of the exchange-correlation density

$$f(\mathbf{r}_1,\mathbf{r}_2) = 2\Gamma(\mathbf{r}_1,\mathbf{r}_2) - \rho(\mathbf{r}_1)\rho(\mathbf{r}_2); \int f(\mathbf{r}_1,\mathbf{r}_2)\, d\mathbf{r}_1\mathbf{r}_2 = -N \quad (2)$$

Then one can define a localization index by integrating the exchange-correlation density within an atom A

$$\lambda(A) = -\int_A \mathbf{f}(\mathbf{r}_1,\mathbf{r}_2)\, d\mathbf{r}_1\, d\mathbf{r}_2 \quad (3)$$

and a delocalization index by integrating each of the $\mathbf{r}_1$ and $\mathbf{r}_2$ coordinates in $f(\mathbf{r}_1,\mathbf{r}_2)$ within the basins of two atoms, A and B

$$\delta(A,B) = -\int_A\int_B \mathbf{f}(\mathbf{r}_1,\mathbf{r}_2)\, d\mathbf{r}_1\, d\mathbf{r}_2 - \int_B\int_A \mathbf{f}(\mathbf{r}_1,\mathbf{r}_2)\, d\mathbf{r}_1\, d\mathbf{r}_2 = -2\int_A\int_B \mathbf{f}(\mathbf{r}_1,\mathbf{r}_2)\, d\mathbf{r}_1\, d\mathbf{r}_2 \quad (4)$$

$\lambda$(A) is the number of electrons that are localized into the atom A. It is always less than the corresponding atomic population, $N$(A), except for totally isolated atoms, where there is no exchange or correlation with electrons in other atoms. The delocalization index, $\delta$(A,B), accounts for the electrons delocalized or shared between the atoms A and B. For bonded atoms, $\delta$(A,B) depends both on the number of electron pairs shared between the atoms and on the particular kind of interaction between these atoms. Thus, $\delta$(A,B) values are large between pairs of atoms with covalent shared interactions, intermediate for polar shared interactions, and very low for closed interactions (ionic, van der Waals, H bonding). Furthermore, nonvanishing electron delocalization can also occur between nonbonded atoms. These kind of interactions can be chemically significant.

Localization and delocalization indices have been calculated for a number of molecules, at the Hartree−Fock (HF) and configuration interaction (CI) levels of theory. It has been shown that, in many cases, the descriptions of electron-pairing provided by means of the Lewis model and the localization and delocalization indices are qualitatively similar, especially at the HF level.[10] Several authors have recently calculated $\lambda$(A) and $\delta$(A,B) values for a number of molecules at the HF[11−13] and density functional theory (DFT)[13−17] levels. However, one must take into account that the $\lambda$(A) and $\delta$(A,B) values calculated at the DFT level in refs 13−17 have been obtained by using the noninteracting second-order density matrix obtained from the Kohn−Sham determinant. Therefore, the indices calculated in this way do not include explicitly electron correlation beyond exchange and should be considered as an approximation to the real values.[18,19] Finally, localization and delocalization indices, calculated at the HF and CISD levels of theory, have been used to study several reactions in gas phase by analyzing in detail the changes in electron pairing that take place along the intrinsic reaction path of each process.[20]

The aim of the present paper is to analyze the effect of the solvent, as described in the PCM method, into the one- and two-electron density distributions of several molecules. The AIM theory mentioned above will be used for this analysis, paying special attention to the changes induced by the solvent into the electron-pairing patterns of the molecules studied. Two different application examples are presented. In both cases, results in vacuo are compared with those obtained with chloroform and water as solvents. First of all, three different isoelectronic molecular series, comprising cationic, neutral, and anionic species, are studied. Then the Menshutkin reaction (MR) between ammonia and methyl chloride is analyzed by calculating the atomic populations and localization indices for each atom and delocalization indices for each pair of atoms at several points along the reaction coordinate, paying special attention to the stationary points corresponding to reactants, transition state, and products. Finally, we carry out a study of this MR with a discrete representation of the solvent and compare the results to those obtained by the PCM method.

**Methodology**

Wave functions in vacuo for the $H_2O$, $NH_3$, and $H_2S$ series, as well as for all the stationary points in the MR, were calculated at the HF/6-31++G* level of theory, using the Gaussian 98 package.[21] In all cases, solvent effects in chloroform ($\epsilon = 4.9$) and water ($\epsilon = 78.39$) solutions were included using the SCRF-MST method. All the molecular structures were fully optimized in vacuo and considering the effect of the two solvents. The intrinsic reaction path (IRP) for the MR, in gas phase and in aqueous solution, have been computed with the Gaussian 98 package, going downhill from the transition state in mass-weighted coordinates.[22] Then the study of the MR by means of the discrete representation of the solvent has been carried out incorporating two water molecules in the description of the model reaction.

At the HF level of theory, localization and delocalization indices can be calculated following this expression:

$$\lambda(A) = -\sum_{i,j}(S_{ij}(A))^2; \delta(A,B) = -2\sum_{i,j} S_{ij}(A)S_{ij}(B) \quad (5)$$

where $S_{ij}$(A) is the overlap of the molecular orbitals (MO) $i$ and $j$ within the basin of atom A. The atomic overlap matrices containing all the pairwise overlaps between the MO's for each atom as well as the atomic electron populations were obtained by means of the Aimpac package.[23] The accuracy of the integrations for any molecule can be assessed by checking that the summation of all the localization and delocalization indices is equal to the number of electrons in the molecule. For all the molecules, the difference is always smaller than $10^{-3}$ au.

The computational methods described above should be accurate enough for a qualitative investigation of the effects of solvation in the electron pairing in molecules. However, one must be aware that there are some inherent limitations associated with the approximations used. First, the SCRF method treats the solvent as a dielectric medium. Therefore, only polarization effects between solvent and solute are taken into account. No transfer of charge nor electron delocalization between solute and solvent is allowed. Specific solute−solvent interactions, i.e., H-bonding between solute and water molecules, cannot be taken into account by means of the PCM method. For that reason, we decided to study the reaction also using a simple discrete representation of the solvent, which allows us to analyze the electron delocalization between solute and solvent. Second, the HF method tends to overemphasize the interatomic delocalization of the electrons, especially between atoms that are covalently bonded. For instance, for diatomic homonuclear molecules, each electron pair shared between the two atoms contributes with exactly 1 to the total delocalization index at the HF level. At the CI level, it has been found that the contribution of each shared electron pair is usually between 0.7 and 0.9 for these molecules.[10]

The Gaussian 98[21] builds up the solvation cavity by putting a sphere around each solute heavy atom, where the hydrogens atoms bonded to it are enclosed. The radii of these spheres are multiplied by a scale factor which is 1.20 for water and 1.40

**TABLE 1: Relative Energies with Respect to the Gas Phase ($\Delta E$), Interatomic Distances ($r$), Interatomic Angles ($\alpha$), Atomic Populations ($N$), and Localization ($\lambda$) and Delocalization ($\delta$) Indices for the Molecules in the Three Series Studied, Calculated in Vacuo, in Chloroform, and in Water[a]**

(a) $OH^-$, $H_2O$, and $H_3O^+$

| | $OH^-$ | | | $H_2O$ | | | $H_3O^+$ | | |
|---|---|---|---|---|---|---|---|---|---|
| | in vacuo | chlorof. | water | in vacuo | chlorof. | water | in vacuo | chlorof. | water |
| $\Delta E$[b] | 0.0 | −74.7 | −111.7 | 0.0 | −2.5 | −7.5 | 0.0 | −68.4 | −107.9 |
| $r$ | 0.954 | 0.950 | 0.970 | 0.948 | 0.950 | 0.955 | 0.969 | 0.976 | 0.995 |
| $\alpha$ | | | | 106.5 | 105.9 | 105.6 | 112.4 | 110.2 | 109.4 |
| $N$(O) | 9.436 | 9.508 | 9.614 | 9.200 | 9.225 | 9.266 | 9.196 | 9.211 | 9.261 |
| $N$(H) | 0.564 | 0.492 | 0.386 | 0.400 | 0.387 | 0.367 | 0.268 | 0.263 | 0.246 |
| $\lambda$(O) | 9.008 | 9.120 | 9.294 | 8.554 | 8.594 | 8.660 | 8.505 | 8.530 | 8.616 |
| $\lambda$(H) | 0.136 | 0.105 | 0.066 | 0.073 | 0.069 | 0.062 | 0.034 | 0.033 | 0.029 |
| $\delta$(O,H) | 0.856 | 0.775 | 0.640 | 0.647 | 0.631 | 0.605 | 0.461 | 0.454 | 0.430 |
| $\delta$(H,H) | | | | 0.007 | 0.006 | 0.006 | 0.004 | 0.003 | 0.003 |

(b) $NH_2^-$, $NH_3$, and $NH_4^+$

| | $NH_2^-$ | | | $NH_3$ | | | $NH_4^+$ | | |
|---|---|---|---|---|---|---|---|---|---|
| | in vacuo | chlorof. | water | in vacuo | chlorof. | water | in vacuo | chlorof. | water |
| $\Delta E$[c] | 0.0 | −64.6 | −96.0 | 0.0 | −1.9 | −5.0 | 0.0 | −54.6 | −80.3 |
| $r$ | 1.019 | 1.013 | 1.016 | 1.002 | 1.003 | 1.005 | 1.013 | 1.014 | 1.018 |
| $\alpha$ | 103.5 | 104.1 | 107.0 | 108.0 | 107.4 | 107.2 | 109.5 | 109.5 | 109.5 |
| $N$(N) | 8.399 | 8.487 | 8.650 | 8.147 | 8.169 | 8.217 | 8.171 | 8.177 | 8.198 |
| $N$(H) | 0.801 | 0.756 | 0.675 | 0.618 | 0.610 | 0.595 | 0.457 | 0.456 | 0.450 |
| $\lambda$(N) | 7.361 | 7.482 | 7.709 | 6.855 | 6.886 | 6.953 | 6.777 | 6.786 | 6.819 |
| $\lambda$(H) | 0.269 | 0.242 | 0.195 | 0.172 | 0.168 | 0.160 | 0.099 | 0.098 | 0.096 |
| $\delta$(N,H) | 1.037 | 1.005 | 0.940 | 0.861 | 0.855 | 0.842 | 0.697 | 0.695 | 0.690 |
| $\delta$(H,H) | 0.027 | 0.025 | 0.020 | 0.015 | 0.014 | 0.014 | 0.007 | 0.007 | 0.007 |

(c) $SH^-$, $H_2S$, and $H_3S^+$

| | $SH^-$ | | | $H_2S$ | | | $H_3S^+$ | | |
|---|---|---|---|---|---|---|---|---|---|
| | in vacuo | chlorof. | water | in vacuo | chlorof. | water | in vacuo | chlorof. | water |
| $\Delta E$[d] | 0.0 | −52.1 | −74.0 | 0.0 | 0.0 | −0.6 | 0.0 | −56.5 | −87.2 |
| $r$ | 1.340 | 1.335 | 1.333 | 1.327 | 1.327 | 1.328 | 1.331 | 1.335 | 1.357 |
| $\alpha$ | | | | 94.4 | 94.5 | 94.9 | 96.9 | 97.0 | 96.8 |
| $N$(S) | 16.863 | 16.889 | 16.968 | 16.014 | 16.036 | 16.079 | 15.563 | 15.629 | 15.818 |
| $N$(H) | 1.138 | 1.112 | 1.032 | 0.993 | 0.982 | 0.961 | 0.813 | 0.790 | 0.732 |
| $\lambda$(S) | 16.261 | 16.292 | 16.382 | 14.933 | 14.958 | 15.006 | 14.102 | 14.183 | 14.422 |
| $\lambda$(H) | 0.536 | 0.513 | 0.447 | 0.437 | 0.427 | 0.410 | 0.308 | 0.291 | 0.250 |
| $\delta$(S,H) | 1.204 | 1.197 | 1.171 | 1.081 | 1.078 | 1.073 | 0.973 | 0.964 | 0.934 |
| $\delta$(H,H) | | | | 0.031 | 0.031 | 0.029 | 0.018 | 0.017 | 0.015 |

[a] Energies in kcal mol$^{-1}$, populations in au (electrons), distances in Å, and angles in deg. [b] Absolute energies for the molecules in gas phase: $OH^-$, −75.37668 au; $H_2O$, −76.01789 au; $H_3O^+$, −76.29103 au. [c] Absolute energies for the molecules in gas phase: $NH_2^-$, −55.51857 au; $NH_3$, −56.18991 au; $NH_4^+$, −56.53188 au. [d] Absolute energies for the molecules in gas phase: $HS^-$, −398.10699 au; $H_2S$, −398.66823 au; $H_3S^+$, −398.94288 au.

for chloroform. With respect to the radii used in each of the three systems studied at the first part, $OH^-$, $H_2O$, and $H_3O^+$, $NH_2^-$, $NH_3$, and $NH_4^+$, and $HS^-$, $H_2S$, and $H_3S^+$ , these are 1.290, 1.680, and 1.510, 1.480, 1.770, and 1.770, and 1.810, 2.240, and 1.820 Å, respectively. On the other hand, the radii for the species of the Menshutkin reaction are 2.040 ($CH_3$), 1.980 (Cl) and 1.770 ($NH_3$) for the reactants, 1.770 ($NH_3$), 1.950 ($CH_3$) and 1.680 (Cl) for the TS, 1.770 ($NH_3$), 1.950 ($CH_3$) and 1.680 (Cl) for the product complex (only obtained with chloroform), and 1.680 ($Cl^-$), 1.770 ($NH_3$) and 1.950 ($CH_3$) Å for the products.

## Results and Discussion

**A. Analysis of Three Series of Anionic, Neutral, and Cationic Species.** Table 1 contains the results for the nine molecules considered in this section. These are grouped into three series: $OH^-$, $H_2O$, and $H_3O^+$; $NH_2^-$, $NH_3$, and $NH_4^+$; and $HS^-$, $H_2S$, and $H_3S^+$. Alternatively, these molecules can be separated into neutral, anionic, and cationic species. Therefore, both the effects of the solvent in the three series and the different effects of solvation in neutral molecules, anions, and cations will be analyzed.

First of all, we comment briefly on the results obtained in vacuo for the three neutral molecules ($H_2O$, $NH_3$, and $H_2S$). Indeed, localization and delocalization indices have already been reported for these molecules at the HF level, with different basis sets (6-311++G(2d,2p)[10] and DZVP[12]). The results reported in Table 1 (6-31++G*) are consistent with those reported in refs 10 and 11. The AIM analysis reveals that for $H_2O$ and $NH_3$, each H atom transfers ca. 0.6 and 0.4 electrons to the O and N atoms, respectively. Moreover, $\lambda$(H) is quite low in both cases (18% and 28% of the electron population in H, respectively). Finally, $\delta$(O,H) and $\delta$(N,H) are 0.65 and 0.86, respectively, which are characteristic of shared polar interactions, with the bonds of $H_2O$ being more polar than the $NH_3$ ones. In contrast, the S−H interaction in $H_2S$ appears to be clearly covalent: there is no apreciable transfer of charge between the two atoms, and $\delta$(S,H) is very close to 1 (1.081).

For the two molecules with more polar bonds, $H_2O$ and $NH_3$, the subtraction of a proton to yield the $OH^-$ and $NH_2^-$ anions increases the delocalization of the O−H and N−H interactions. In contrast, the bonds of the $H_3O^+$ and $NH_4^+$ cations are more localized than those of the corresponding neutral molecules, $H_2O$ and $NH_3$, respectively. This trend is made evident in the

delocalization indices in the two series: $\delta$(O,H) is 0.86, 0.65, and 0.46 for the $OH^-$, $H_2O$, and $H_3O^+$ molecules, respectively, while $\delta$(N,H) is 1.04, 0.86, and 0.70 for $NH_2^-$, $NH_3$, and $NH_4^+$, respectively. Similar trends are found for the atomic populations and the localization indices. Finally, the $SH^-$, $H_2S$, and $H_3S^+$ series exhibits some interesting trends. First, the S−H interactions in $H_2S$ and $H_3S^+$ appear to be quite similar. For instance, the positive electron charge in $H_3S^+$ is distributed evenly between S (+0.44) and the three H atoms (+0.19 each). Moreover, $\delta$(S,H) in $H_3S^+$ remains close to 1 (0.97). For $SH^-$, the negative charge is located mainly in the S atom (−0.86). However, $\delta$(S,H) increases to a value of 1.2 in this molecule. Since the maximal $\delta$(A,B) value for a pair of electrons shared between two atoms is 1, it is clear that more than one pair of electrons is contributing to the delocalization between these two atoms. Indeed, an analysis of the $\sigma$ and $\pi$ contributions to $\delta$(S,H) reveals that there is a total $\pi$ contribution of 0.182 e, while the contribution of the $\sigma$ electrons is 1.022. Indeed, the three lone-pair electrons in S, which are represented in part by diffuse sp orbitals which extend into the H basin, account for the interatomic delocalization of the $\pi$ electron density. However, the $\sigma$ contribution to the delocalization index is still slightly larger than 1, which is probably due to a small delocalization of the S core electrons into the H atom. The fact that $H_2S$ has a $\delta$(S,H) value of 1.081 can also be related mainly to the delocalization of the two lone electron pairs in this molecule. However, since $H_2S$ is not linear, an exact separation of the $\sigma$ and $\pi$ contributions to $\delta$(S,H) is not possible in this case.

Once the electronic structure of these molecules in vacuo has been described, we proceed to analyze the effects of solvation in chloroform and water. From an energetic point of view, all the molecules are more stable in solution than in the gas phase. In all cases, the stabilization is significantly larger in water than in chloroform. For the three neutral molecules, the solvation energy is quite small, especially for $H_2S$. For the $H_2O$ and $NH_3$ series, solvation in water or chloroform is more favorable for the anion than for the cation, while the reverse trend is found in the $H_2S$ series.[24] The larger polarizability of the S atom may explain the differences between the stabilization energy for the anion and the cation in the $H_2S$ series as compared to those in the $H_2O$ and $NH_3$ series. In general, for neutral and cationic species, solvation in water leads to larger bond distances between the heavy atoms and the H atoms. On the other hand, for anions, solvation shortens the bonds, as it leads to a notable shrinking in molecular volume due to the concentration of charge density from outer to inner regions of molecules, which increases the solute−solvent interaction, leading to a better solvation.[6] It be must be noted that $OH^-$ does not follow this behavior in the present study. Additional calculations with the high level ab initio CCSD(T) method and larger basis sets have shown that the effect is not due to a limitation of the method or the basis set. The standard cavity generated by Gaussian 98 locates a sphere on each heavy atom but not in hydrogen atoms. To see if this may be the origin of the anomalous behavior of $OH^-$, we performed further PCM calculations with Gaussian 98 with sphere radii provided externally ($r_O$ = 1.40 Å and $r_H$ = 1.20 Å). In that way, the program generates the cavity, locating a sphere on both the oxygen and the hydrogen atoms. In this case, we have reproduced the usual behavior found in anions, and we have observed the expected decrease in bond length. Therefore, we can attribute the abnormal behavior of $OH^-$ to the particular way in which the Gaussian 98 program builds up the solvation cavity.

The comparison of the N, $\lambda$, and $\delta$ values for the calculations in vacuo and in solvation reveals some trends shared for all the molecules and both solvents. Thus, solvation increases the transfer of charge from H to the heavy atom and increases the electron localization in the O, N, and S atoms at the same time that $\lambda$(H) and the delocalization between heavy atoms and H atoms decrease. All these trends are consistent with an increased polarization of the bonds of the molecules in solvation, in agreement with previous observations.[6,8] However, the main characteristics of the electronic pairing of the molecules in gas phase are conserved in solvation, especially for the neutral and cationic species. As expected, this polarization is stronger with water as the solvent than with chloroform, and it is much more important for the anionic species than for the corresponding neutral and cationic species. In general, the electron-pairing rearrangements induced by chloroform on neutral molecules and cations are negligible.

The fact that solvent effects on electron pairing are generally more important for anionic species is in agreement with their larger energetic stabilization and their larger associated polarization values. On the other hand, solvation induces similar electron-pair changes to the neutral and cationic species, despite the larger energetic stabilization being associated with the solvation of the latter. This can be attributed to the fact that cations are less polarizable and electron redistribution in these species is more difficult.

**B. Analysis of the $CH_3Cl + NH_3 \rightarrow Cl^- + CH_3NH_3^+$ Menshutkin Reaction.** *Gas-Phase Results.* The Menshutkin reaction[25,26] is a special type of $S_N2$ reaction, where two neutral molecules react to yield two charged products, in contrast to the usual $S_N2$ reactions, where one of the reactants is charged. Thus, in MRs, two ions of opposite charge are created and progressively separated during the reaction, a process which is unfavorable in gas phase, due to attractive Coulombic interactions between the two ions. However, this reaction is more favorable in solvation, especially in polar solvents, due to the larger stabilization of the transition state (TS) and products than of the reactants. Therefore, MRs make an excellent target for assessing the effects of solvation on the PES of a chemical reaction.[27,28]

The original study by Menshutkin focused on the reaction between triethylamine with ethyl iodine, using 22 different solvents.[25] Later, several experimental studies have considered different solvents, nucleophiles, and leaving groups (see ref 26 for a review). Here, we consider the model reaction between ammonia and methyl chloride to form methylammonium and a chlorine anion. The influence of external perturbations in the PES of this reaction, namely, electric fields and solvents, has already been investigated at the HF/3-21+G* level of theory.[7] Therefore, the aim of this section is to complement the results in ref 7 by analyzing for the first time the effects of the solvent on the electron-pair distribution along the reaction path.

The energy profile of this MR in gas phase consists of an asymmetric double-well potential with five stationary points, corresponding to reactants (R), reactant complex (RC), transition state (TS), product complex (PC), and separated ionic products (P). Both theoretical and experimental studies have found this reaction to be highly endothermic in gas phase, with an experimental reaction energy larger than 100 kcal $mol^{-1}$.[28−30] Electric fields and solvents stabilize the TS, decreasing the height of the reaction barrier.[28] From a structural point of view, these external perturbations lead to an advance of the TS in the reaction path—that is, the TS becomes more "reactant-like".[7,28−30]

**TABLE 2: Relative Energies Referring to the Separated Reactants ($\Delta E$), Interatomic Distances between C and Cl ($r_{CCl}$) and C and N ($r_{CN}$), Distinguished Reaction Coordinates Defined as $R_x = r_{CCl} - r_{CN}$, Atomic Populations ($N$), and Localization ($\lambda$) and Delocalization ($\delta$) Indices for the Reactants (R), Reactant Complex (RC), Transition State (TS), Product Complex (PC), and Products (P) of the Menshutkin Reaction, Calculated in Vacuo (a), in Chloroform (b), and in Water (c)[a]**

(a) In Vacuo

| | R | RC | TS | PC | P |
|---|---|---|---|---|---|
| $\Delta E^b$ | 0.0 | −1.7 | 36.2 | 28.9 | 106.1 |
| $r_{CCl}$ | 1.786 | 1.793 | 2.472 | 2.918 | ∞ |
| $r_{CN}$ | ∞ | 3.547 | 1.901 | 1.542 | 1.507 |
| $r_{CCl} - r_{CN}$ | −∞ | −1.754 | 0.571 | 1.376 | ∞ |
| $N$(N) | 8.147 | 8.153 | 8.132 | 8.175 | 8.210 |
| $N$(C) | 5.823 | 5.811 | 5.805 | 5.705 | 5.637 |
| $N$(Cl) | 17.322 | 17.347 | 17.814 | 17.939 | 18.000 |
| $N$($H_N$) | 0.618 | 0.615 | 0.554 | 0.515 | 0.486 |
| $N$($H_C$) | 0.952 | 0.948 | 0.862 | 0.879 | 0.898 |
| $\lambda$(N) | 6.855 | 6.840 | 6.616 | 6.584 | 6.640 |
| $\lambda$(C) | 3.874 | 3.866 | 3.989 | 3.879 | 3.816 |
| $\lambda$(Cl) | 16.702 | 16.736 | 17.541 | 17.811 | 18.000 |
| $\lambda$($H_N$) | 0.172 | 0.171 | 0.140 | 0.123 | 0.111 |
| $\lambda$($H_C$) | 0.413 | 0.409 | 0.336 | 0.347 | 0.374 |
| $\delta$(N,C) | 0.000 | 0.020 | 0.498 | 0.767 | 0.818 |
| $\delta$(N,$H_N$) | 0.861 | 0.859 | 0.791 | 0.745 | 0.717 |
| $\delta$(C,Cl) | 1.043 | 1.026 | 0.348 | 0.110 | 0.000 |
| $\delta$(C,$H_C$) | 0.952 | 0.948 | 0.920 | 0.913 | 0.930 |
| $\delta$(Cl,$H_C$) | 0.065 | 0.064 | 0.048 | 0.042 | 0.000 |

(b) Chloroform

| | R | TS | PC | P |
|---|---|---|---|---|
| $\Delta E^c$ | 0.0 | 24.5 | −3.1 | 5.6 |
| $r_{CCl}$ | 1.788 | 2.359 | 3.191 | ∞ |
| $r_{CN}$ | ∞ | 2.064 | 1.508 | 1.495 |
| $r_{CCl} - r_{CN}$ | −∞ | 0.295 | 1.683 | ∞ |
| $N$(N) | 8.169 | 8.162 | 8.213 | 8.225 |
| $N$(C) | 5.827 | 5.807 | 5.630 | 5.611 |
| $N$(Cl) | 17.341 | 17.783 | 17.974 | 18.000 |
| $N$($H_N$) | 0.610 | 0.558 | 0.490 | 0.478 |
| $N$($H_C$) | 0.944 | 0.857 | 0.905 | 0.910 |
| $\lambda$(N) | 6.886 | 6.697 | 6.640 | 6.661 |
| $\lambda$(C) | 3.884 | 4.005 | 3.797 | 3.782 |
| $\lambda$(Cl) | 16.728 | 17.475 | 17.899 | 18.000 |
| $\lambda$($H_N$) | 0.168 | 0.142 | 0.112 | 0.107 |
| $\lambda$($H_C$) | 0.407 | 0.334 | 0.373 | 0.383 |
| $\delta$(N,C) | 0.000 | 0.388 | 0.804 | 0.827 |
| $\delta$(N,$H_N$) | 0.855 | 0.799 | 0.720 | 0.708 |
| $\delta$(C,Cl) | 1.033 | 0.431 | 0.062 | 0.000 |
| $\delta$(C,$H_C$) | 0.951 | 0.922 | 0.922 | 0.931 |
| $\delta$(Cl,$H_C$) | 0.065 | 0.045 | 0.026 | 0.000 |

(c) Water

| | R | TS | P |
|---|---|---|---|
| $\Delta E^d$ | 0.0 | 16.1 | −35.1 |
| $r_{CCl}$ | 1.793 | 2.274 | ∞ |
| $r_{CN}$ | ∞ | 2.181 | 1.487 |
| $r_{CCl} - r_{CN}$ | −∞ | 0.093 | ∞ |
| $N$(N) | 8.217 | 8.192 | 8.248 |
| $N$(C) | 5.837 | 5.829 | 5.593 |
| $N$(Cl) | 17.364 | 17.762 | 18.000 |
| $N$($H_N$) | 0.595 | 0.559 | 0.466 |
| $N$($H_C$) | 0.933 | 0.846 | 0.920 |
| $\lambda$(N) | 6.953 | 6.763 | 6.696 |
| $\lambda$(C) | 3.903 | 4.037 | 3.758 |
| $\lambda$(Cl) | 16.757 | 17.427 | 18.000 |
| $\lambda$($H_N$) | 0.160 | 0.142 | 0.102 |
| $\lambda$($H_C$) | 0.398 | 0.326 | 0.391 |
| $\delta$(N,C) | 0.000 | 0.316 | 0.838 |
| $\delta$(N,$H_N$) | 0.842 | 0.802 | 0.695 |
| $\delta$(C,Cl) | 1.021 | 0.491 | 0.000 |
| $\delta$(C,$H_C$) | 0.949 | 0.920 | 0.933 |
| $\delta$(Cl,$H_C$) | 0.064 | 0.043 | 0.000 |

[a] $H_N$ and $H_C$ refer to the H atoms bonded to N and C, respectively. Energies in kcal mol$^{-1}$, populations in au (electrons), and distances in Å. [b] Reference energy for the reactants: −555.28428 au. [c] Reference energy for the reactants: −555.28770 au. [d] Reference energy for the reactants: −555.29338 au.

Table 2 gathers all the data relevant to the MR studied, including the value of the reaction coordinate for the different stationary points. It must be noticed that the term reaction coordinate has two meanings in this paper: first, it stands for what some authors call distinguished reaction coordinate, in this case the difference between $r_{CCl}$ and $r_{CN}$ (given in Tables); second, it has a more precise sense representing the advance of the reaction from reactants to products involving the full set of geometrical parameters which define the reactant systems, that is, the so-called intrinsic reaction coordinate (IRC). The energy profiles in vacuo (Table 2a) and in water (Table 2c) are similar to those calculated with the 3-21+G* basis set,[7] with the difference being that the minima corresponding to reactant and product complexes in water were not found with the small basis set. The reaction energy calculated at the HF/6-31++G* level of theory (106.1 kcal mol$^{-1}$) is in good agreement with previous theoretical calculations[7,31−33] and with reported experimental values (110 ± 5 [29] and 127.2 [30] kcal mol$^{-1}$). The activation energy calculated in this work (36.2 kcal mol$^{-1}$) is also close to the results of previous theoretical studies. For instance, several authors have obtained values between 32.6 and 38.6 kcal mol$^{-1}$ for the activation energy of this reaction,[30−32] using different ab initio methods and basis sets of quality comparable to the 6-31++G*.

For the MR in gas phase, the evolution of the electronic structure, from reactants to products, can be followed by discussing the electron pairing in the structures corresponding to the five stationary points characterized in the reaction path. In the $CH_3Cl$ molecule, the Cl atom has a charge of −0.32. Both the C−H and C−Cl bonds can be considered as covalent, with the corresponding delocalization indices close to 1. As for the $NH_3$ molecule, the AIM analysis reveals that the N−H bonds are clearly polar, as discussed above. Going from the R to the RC, there is a slightly increased charge transfer (0.025 e) from the $CH_3$ group toward the Cl atom, while the total charge in the $NH_3$ group remains at zero. The interaction between the two molecules in the complex is weak, as revealed by the large C−N distance (3.55 Å) and the small value of $\delta$(C,N) (0.02). In the product molecule $CH_3NH_3^+$, the C−H and N−H bonds are more polar than the corresponding bonds in the reactant molecules, and the C−N bond formed during the reaction is also strongly polarized toward N. For instance, the N atom has a charge of −1.21, while C, $H_C$, and $H_N$ have charges of +0.36, +0.20, and +0.51, respectively. According to the delocalization indices, C−H interactions are still near to the covalent limit ($\delta$(C,H) = 0.93), while C−N and N−H interactions are polarized toward the heavy atoms ($\delta$(C,N) = 0.82, $\delta$(N,H) = 0.72). These two molecules retain their main electron-pair characteristics in the PC. At this point, the charge transfer is nearly complete, the Cl, $CH_3$, and $NH_3$ groups having charges of −0.94, +0.66, and +0.28, the electron delocalization between Cl and other atoms being small.

According to the data discussed in the paragraph above, the main changes in the electron density and electron-pair distribution needed to evolve from the RC to the PC are (i) the transfer of 0.59 e from the $CH_3$ and $NH_3$ groups to the Cl atom, (ii) the decreasing importance of the C−Cl interaction at the same time that the C−N interaction increases, and (iii) the increasing polarity of the C−H and N−H interactions. Charge transfer (point i) is reflected on the atomic populations, especially N(Cl), while points ii and iii are reflected mainly on the delocalization indices $\delta$(N,C), $\delta$(C,Cl), $\delta$(C,H), and $\delta$(N,H). The analysis of these data reveals that, from a first-order density and electron-pair perspective, the TS is closer to the PC than to the RC. First, the Cl, $CH_3$, and $NH_3$ groups exhibit charges of −0.81, +0.61, and +0.21, respectively. Thus, the transfer of charge

from the $CH_3NH_3$ group to the Cl atom, which is of 0.35 and 0.94 e at the RC and PC, respectively, is quite advanced toward the PC at this point. Moreover, the $\delta$(N,C) and $\delta$(C,Cl) values are 0.50 and 0.35, respectively, which are intermediate between those at the reactant and product complexes but closer to the PC (0.77 and 0.11, respectively) than to the RC (0.02 and 1.03, respectively). The variation of $\delta$(C,H) and $\delta$(N,H) along the reaction is small; however, the values at the TS are significantly closer to those at the PC than to those at the RC. Finally, most of the localization indices at the TS have intermediate values between the corresponding values at the reactant and product complexes but closer to the PC. The only exceptions are $\lambda$(C) and $\lambda(H_C)$, which are maximal and minimal, respectively, at the TS, still closer to the PC than to the RC. All in all, the TS in gas phase has an electron-pair structure quite similar to that of the PC. In terms of molecular geometry, the TS is also close to the PC (see the distinguished reaction coordinate values in Table 2a), in agreement with the Hammond postulate,[34] which states that the TS should be "product-like" for endothermic reactions.

*Continuum Representation of the Solvent.* Parts b and c of Table 2 gather the results for the studied MR in chloroform and in aqueous solution, respectively. It must be mentioned that neither the RC in chloroform nor the RC and PC in water are stationary points in the PES computed at the HF/6-31++G* level of theory. Results in Table 2 point out that the effects of solvation in the R are weak. Solvation tends to enhance the polarity of the bonds by increasing the atomic populations and localization indices for the N and Cl atoms and decreasing them for the H atoms. Moreover, all delocalization indices between bonded atoms also decrease slightly. These effects are very small for water, and practically negligible for chloroform. As expected, solvation effects are more important for the P, formed by two charged species. Aqueous solvation leads to some redistribution of charge from $CH_3$ to $NH_3$ and Cl. Accordingly, electron localization also decreases for $CH_3$ and increases for $NH_3$ and Cl. As for the delocalization indices, the most remarkable is that solvation increases $\delta$(N,C) from 0.82 to 0.84, despite increasing the differences between the atomic populations in those atoms. $\delta$(C,H) also increases slightly, while the rest of delocalization indices decrease, especially $\delta$(N,H). Solvation in chloroform produces equivalent changes, but smaller in magnitude.

Solvation induces important changes in the molecular structure and the electron-pairing characteristics of the TS. In agreement with previous studies,[7,28−30] we have found that the TS in solution moves toward the reactant side, as expected in the light of the Hammond postulate for a reaction that becomes less endothermic. From the point of view of the atomic populations, solvation in water decreases the charge in Cl and $NH_3$ by 0.05 and 0.08 e, respectively, while it increases the charge in the $CH_3$ group by 0.02 e, making the TS more "reactant-like". However, comparison of the electron charges in Cl at the R (−0.36), TS (−0.76), and P (−1.00) reveals that the TS is still more similar to the P than to the R in terms of charge transfer. Changes in the localization indices are similar to those found for the electron charges: solvation decreases the electron localization in the Cl atom and increases it in the $CH_3$ and $NH_3$ groups. However, the main effects of solvation are found in $\delta$(N,C), which decreases from 0.50 to 0.32, and $\delta$(C,Cl), which increases from 0.35 to 0.49. $\delta$(N,H) also increases slightly, from 0.79 to 0.80, while $\delta$(C,H) does not change at all. According to these changes, the effect of aqueous solvation is to move the TS structurally and electronically toward the reactant side of the reaction path. In fact, according to $\delta$(N,C), the TS (0.32) in water is much closer to the R (0.00) than to the P (0.84). However, $\delta$(C,Cl) at the TS (0.49) is practically midway between the R (1.02) and the P (0.00). The effects of solvation in chloroform are very similar to those described above for water, both in terms of charge transfer and electron delocalization. The only difference is that solvent effects on the TS are more important for water. Thus, after solvation in water or chloroform, the TS is "product-like", according to the charge in the Cl atom and $\delta$(C,Cl), but "reactant-like" according to $\delta$(N,C).

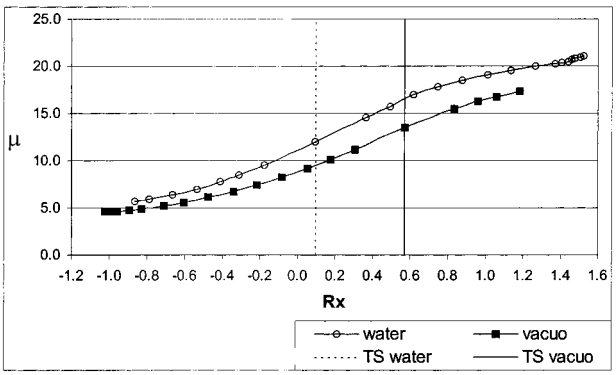


**Figure 1.** Evolution of the dipole moment along the intrinsic reaction path of the $CH_3Cl + NH_3 \rightarrow Cl^- + CH_3NH_3^+$ Menshutkin reaction, both in vacuo and in a continuum representation of the solvent (water), calculated at the HF/6-31++G* level of theory. Negative and positive values of the distinguished reaction coordinate, defined as $R_x = r_{CCl} - r_{CN}$, correspond to reactant and product, respectively.

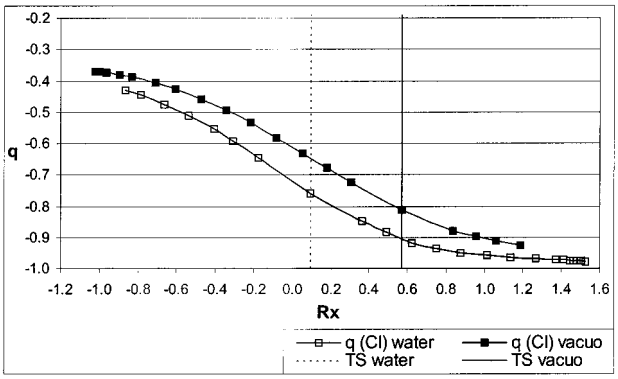


**Figure 2.** Evolution of the Bader's charge on chlorine along the intrinsic reaction path of the $CH_3Cl + NH_3 \rightarrow Cl^- + CH_3NH_3^+$ Menshutkin reaction, both in vacuo and in a continuum representation of the solvent (water), calculated at the HF/6-31++G* level of theory. Negative and positive values of the distinguished reaction coordinate, defined as $R_x = r_{CCl} - r_{CN}$, correspond to reactant and product, respectively.

Figures 1 and 2 show the change in the dipole moment and the evolution of the Bader's charge on chlorine along the intrinsic reaction path. The use of the $R_x = r_{CCl} - r_{CN}$ distinguished reaction coordinate instead of the intrinsic reaction coordinate in the representation allows comparison of the reaction in gas phase and in solution. These figures reval that the solvent induces a significant rearrangement of the solute charge distribution. As found before,[6] this rearrangement shifts electron density from electropositive to electronegative atoms, resulting in an increase in the molecular dipole. Density difference plots between the gas phase and water densities reveal that in solvation, the electron density increases around the two more electronegative atoms, N and Cl, and decreases in the hydrogens bonded to N and C (Figure not shown). Such a rearrangement favors the charge transfer from the ammonia

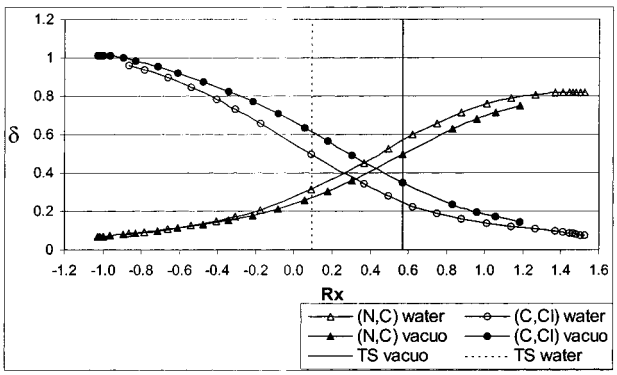


**Figure 3.** Evolution of the values of delocalization indices along the intrinsic reaction path of the $CH_3Cl + NH_3 \rightarrow Cl^- + CH_3NH_3^+$ Menshutkin reaction, both in vacuo and in a continuum representation of the solvent (water), calculated at the HF/6-31++G* level of theory. Negative and positive values of the distinguished reaction coordinate, defined as $R_x = r_{CCl} - r_{CN}$, correspond to reactant and product, respectively.

molecule and the methyl group to chlorine, thus catalyzing the MR. Remarkably, because of the advancement of the TS in solution, the values for the dipole moment obtained at both transition states are very close, 13.5 and 11.9 D in vacuo and in aqueous solution, respectively. A similar trend is found for the charges on Cl, which are −0.81 and −0.76 for the TS in vacuo and in water, respectively.

Further insight on the charge redistribution processes taking place along the MR can be obtained by following the evolution of the electron-pair reorganization along the reaction path. Figure 3 illustrates the evolution of the delocalization indices along the reaction path in vacuo and in aqueous solution. Only $\delta$(N,C) and $\delta$(C,Cl) are depicted in Figure 3, as they account for most part of the electron-pair reorganization taking place during the reaction. Both in vacuo and in aqueous solution, the electron-pair reorganization occurs gradually along the reaction path—that is, there is a large region in the IRP where there is a significant N−C and C−Cl delocalization at the same time. As can be seen, solvation increases the delocalization between N and C and decreases it between C and Cl, which is translated into a stronger N−C bond and a weaker C−Cl bond. The main difference between the curves in vacuo and in solution is that the crossing between the $\delta$(N,C) and $\delta$(C,Cl) indices, at $R_x$ about 0.4 and 0.3 Å, respectively, takes place before the TS in vacuo and after the TS in water solution because of the more advanced position of the TS in solution toward the reactant side. Interestingly, the values of $\delta$(C,Cl) and $\delta$(N,C) are quite different for the TS in vacuo and in solution. This is in contrast to the trend found previously for the dipole moments and atomic charges, which are properties derived from the one-electron density.

Finally, to get deeper insight about the effect of solvation on the electron-pairing in the MR, we have computed the atomic population and localization and delocalization indices in gas phase and in water using the PCM method at the geometry corresponding to the point of the gas-phase intrinsic reaction path with $R_x = r_{CCl} - r_{CN} = 0.306$ Å (point located between the two TS, where a relevant electron-pair redistribution takes place, as can be observed in Figure 3). As said before, solvation increases the atomic populations and localization indices for the N and Cl and decreases them from the hydrogen atoms. As expected from our previous results, solvation decreases $\delta$(C,Cl) from 0.49 to 0.39 e, following the usual behavior for a bond that has increased its polarity. However, contrary to our expectations, the $\delta$(N,C) value increases from 0.36 to 0.42 e, despite that the negative charge on N and the positive charge on C increase when going from the gas phase to solution. The above-mentioned increase of $\delta$(N,C) in solvation can be explained from the analysis of the atomic Fermi hole of the C atom in gas phase and in solution. The atomic Fermi hole[35] is a three-dimensional function which integrates to $-N_A$, the atomic population of atom A, and shows how the electron density of a given atom excludes $N_A$ electrons in the same way that a Fermi or exchange-correlation hole excludes one electron. Figure 4 shows the atomic Fermi hole density contour map of the C atom for the Menshutkin reaction in vacuo (Figure 4a), calculated with the HF approximation, and the atomic Fermi hole density difference contour map between the system in vacuo and in aqueous solution (Figure 4b) at $R_x = r_{CCl} - r_{CN} = 0.306$ Å. It can be already seen that solvation causes an increase of the C Fermi hole next to the nytrogen atom and a decrease next to the chlorine atom. Therefore, $\delta$(N,C) increases because the reduction of the atomic Fermi hole around the Cl atom, created by the reference atomic basin of C, must be compensated by an increase of the same hole in the vicinity of the N atom.

The main conclusion obtained from this analysis is that the solvent, modeled as a continuum dielectric medium, favors the transfer of charge from the ammonia molecule and the methyl group to the chlorine atom, as well as the formation and the breaking of the N−C and C−Cl bonds, respectively, thus facilitating the MR. As a consequence, the TS is electronically and structurally advanced toward the reactant side.

*Discrete Representation of the Solvent.* When the solvent is represented by a continuum model, neither the specific interactions between the solvent and the solute (e.g., hydrogen bonds) nor charge transfer between the solvent and the solute is considered. The aim of this section is to investigate the importance of such effects on the electron-pair distribution of the stationary points in the MR obtained with a discrete representation for the solvent through the supermolecule approach.

In the supermolecule model, practical restrictions limit the number of solvating molecules. In this study, we have considered two water molecules, one solvating chlorine and another solvating ammonia. This is a simple model, but it should be enough to discuss the effect of specific interactions and charge transfer between the solvent and the solute. The water molecule close to ammonia is not hydrogen-bonded to exclusively one of the ammonia hydrogens, but it is placed in a symmetric fashion in such a way that the oxygen of water is aligned along the molecular N−C−Cl axis, interacting simultaneously with all three hydrogens of ammonia. In the optimization process the O, N, C, and Cl atoms, together with a H atom of the water solvating chlorine, were constrained to be collinear (see Figure 5).

Table 3 gathers the most relevant values for the MR studied by a discrete representation of the solvent, corresponding to the reactant complex (RC), the transition state (TS), and the product complex (PC). For the RC, localization and delocalization values hardly change with respect to the model in vacuo. For the PC, solvation effects are more important, as expected from the fact that it is formed by two charged species. Finally, solvation also induces an advance, in terms of electronic and molecular structure, of the TS toward the reactant side of the reaction path. In general, the same trends are found with the PCM and the discrete solvent models; however, solvation effects appear to be smaller using the discrete model with two water molecules. With respect to the molecular geometry (see Figure 5), both

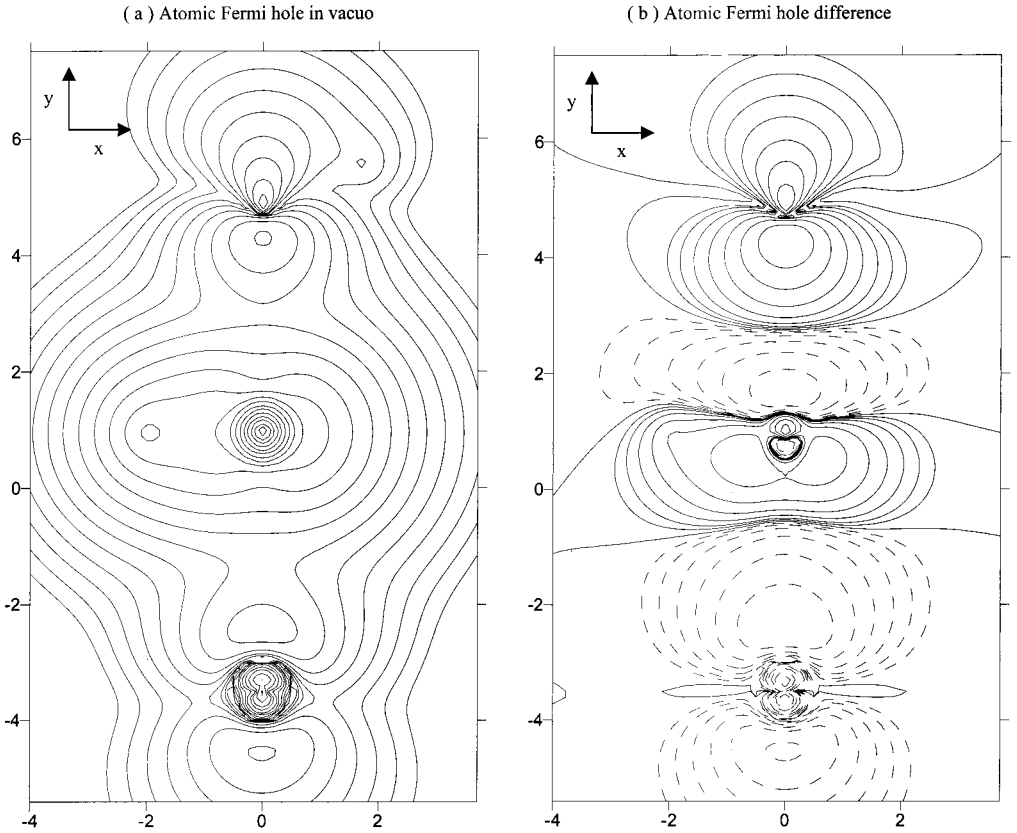


**Figure 4.** Atomic Fermi hole density in vacuo and atomic Fermi hole density difference (vacuo and aqueous solution) contour maps for the C of the $CH_3Cl + NH_3 \rightarrow Cl^- + CH_3NH_3^+$ Menshutkin reaction, calculated with the HF approximation at the geometry corresponding to the point of the gas-phase intrinsic reaction path with $R_x = r_{CCl} - r_{CN} = 0.306$ Å. Isodensity contours at $1 \times 10^{-4}$, $2 \times 10^{-4}$, $4 \times 10^{-4}$, and $8 \times 10^{-4}$ au, etc. In this figure, Cl, C, and N are located at ca. −4, 1, and 5 au, respectively, in the *y*-axis. (a) Atomic Fermi hole in vacuo and (b) atomic Fermi hole difference.

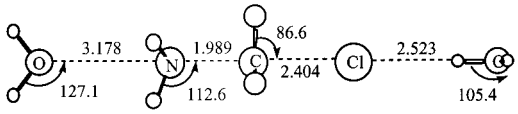


**Figure 5.** Optimized structure for the transition state of the Menshutkin reaction in the discrete representation of the solvent. Bond lengths are given in Å and angles in deg.

the bond distances $r_{CCl}$ and $r_{CN}$ (see Table 3) are very similar to those found with the model in vacuo. The distances between the solvating water molecules and the reacting species get shorter when going from RC to PC.

Finally, electron delocalization between N and the O atom of the water molecule solvating ammonia and between Cl and the H atom of the second water molecule are quite small in all cases. The larger values are obtained for the PC, with $\delta(N,O_w)$ and $\delta(Cl,H_w)$ values of 0.061 and 0.060 e, respectively. In this case, the emerging charges are slightly delocalized over the respective solvating water molecules. In both water molecules, the atomic populations of the O and H are ca. +9.2 and ca. +0.4, respectively, corresponding to charges of ca. −1.2 and ca. +0.6 for the O and H atoms, respectively. Moreover, the total atomic populations of the two water molecules in the PC are 9.98 and 10.03 for the water molecule solvating ammonia and the one solvating chlorine, respectively, corresponding to charge transfers smaller than 0.03 e. This means that there is hardly charge transfer between solute and solvent, a conclusion that was already drawn in previous works[36] on "classical" $S_N2$ reactions such as $CH_3F + Cl^- \rightarrow CH_3Cl + F^-$.

## Conclusions

This study illustrates the effects of solvation in the electronic and molecular structure of several molecules, including neutral, anionic, and cationic species, as well as the stationary points of the MR between methyl chloride and ammonia. We have focused on the changes that take place in the electron pairing of these molecules after solvation. In general, solvation in water or chloroform leads to a polarization of the bonds of these molecules. This polarization is reflected in a larger degree of charge transfer between electronegative and electropositive atoms, an increase of the electron localization for electronegative atoms, and a decrease of the electron delocalization between bonded atoms. Solvation effects are more important for polar (e.g., water) than for apolar (e.g., chloroform) solvents. Moreover, these effects are also more important for charged species, especially anions, than for neutral molecules. For the MR, solvation, especially in water, decreases the activation energy and makes the reaction exothermic. From an electron-pair point of view, the main changes, with respect to the reaction in gas phase, take place in the TS, which is structurally and electronically advanced toward the reactant-side.

In the present study, the PCM method has been used to model the effects of solvation on the solute wave function. The PCM method is able to introduce successfully nonspecific solvent effects at a low computational cost. Indeed, for the MR, results obtained using several variants of the PCM method are in good agreement with more accurate calculations that take into account explicitly solvent molecules. However, within the PCM framework, eventual specific interactions between solute and solvent molecules, e.g., H bonding, cannot be reproduced. For that

**TABLE 3: Relative Energies Referring to the Reactant Complex ($\Delta E$), Interatomic Distances between C and Cl ($r_{CCl}$), C and N ($r_{CN}$), Cl and $H_w$ ($r_{ClH}$), and N and $O_w$ ($r_{NO}$), Distinguished Reaction Coordinate Defined as $R_x = r_{CCl} - r_{CN}$, Atomic Populations ($N$), and Localization ($\lambda$) and Delocalization ($\delta$) Indices for the Reactant Complex (RC), Transition State (TS), and Product Complex (PC) of the Menshutkin Reaction, Calculated in the Discrete Representation of the Solvent[a]**

| | RC | TS | PC |
|---|---|---|---|
| $\Delta E$[b] | 0.0 | 29.2 | 14.7 |
| $r_{CCl}$ | 1.799 | 2.404 | 2.981 |
| $r_{CN}$ | 3.419 | 1.989 | 1.518 |
| $r_{ClH}$ | 3.087 | 2.523 | 2.417 |
| $r_{NO}$ | 3.653 | 3.178 | 2.845 |
| $r_{CCl} - r_{CN}$ | −1.620 | 0.415 | 1.463 |
| $N$(N) | 8.142 | 8.128 | 8.180 |
| $N$(C) | 5.807 | 5.801 | 5.669 |
| $N$(Cl) | 17.373 | 17.782 | 17.925 |
| $N(H_N)$ | 0.617 | 0.562 | 0.514 |
| $N(H_C)$ | 0.941 | 0.861 | 0.890 |
| $N(O_w)$ | 9.209 | 9.225 | 9.244 |
| $N(H_w)$ | 0.393 | 0.368 | 0.356 |
| $\lambda$(N) | 6.813 | 6.618 | 6.565 |
| $\lambda$(C) | 3.871 | 3.993 | 3.839 |
| $\lambda$(Cl) | 16.762 | 17.454 | 17.759 |
| $\lambda(H_N)$ | 0.172 | 0.143 | 0.120 |
| $\lambda(H_C)$ | 0.403 | 0.336 | 0.357 |
| $\lambda(O_w)$ | 8.553 | 8.565 | 8.582 |
| $\lambda(H_w)$ | 0.069 | 0.058 | 0.053 |
| $\delta$(N,C) | 0.026 | 0.436 | 0.786 |
| $\delta(N,H_N)$ | 0.858 | 0.798 | 0.741 |
| $\delta$(C,Cl) | 1.008 | 0.387 | 0.090 |
| $\delta(C,H_C)$ | 0.946 | 0.922 | 0.915 |
| $\delta(Cl,H_C)$ | 0.063 | 0.046 | 0.037 |
| $\delta(N,O_w)$ | 0.022 | 0.040 | 0.061 |
| $\delta(Cl,H_w)$ | 0.009 | 0.043 | 0.060 |

[a] $H_N$ and $H_C$ refer to the H atoms bonded to N and C, respectively, while $O_w$ refers to the O atom of the water solvating the ammonium moiety and $H_w$ to the H of the water molecule which is hydrogen-bonded to Cl. Energies in kcal mol$^{-1}$, populations in au, and distances in Å. [b] Reference energy for the reactant complex: −707.32591 au.

reason, we have applied this analysis to a calculation of the MR with the explicit representation of two solvent molecules. In this way, solute−solvent interactions have been characterized in terms of charge transfer and electron delocalization. We have found that there is nearly no charge transfer and only very small electron delocalization between solute and water, the latter increasing with the reaction coordinate. Furthermore, the effects of solvation in the solute are similar, although different in magnitude, using both the continuum and discrete solvent models. These values confirm the validity of the PCM model for this reaction.

In summary, localization and delocalization indices reflect precisely the effects of solvation on the one- and two-electron density. For the MR, this kind of analysis allows one to follow in detail the changes in electron-pair structure that take place along the reaction, both in the gas phase and in solvation. In general, results in the present and previous papers[10−20] show that localization and delocalization indices, together with atomic populations, are useful descriptors to understand molecular structure and electron redistribution in chemical reactions.

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