influenced by the steric hindrance between the quinone imine and aniline segments.

The introduction of an acetylamino group at the 2-position in the aniline ring produced a specific effect on the absorption properties, which could be explained on the basis of electronic factors and steric effects: (1) the intramolecular hydrogen bond between the imino nitrogen and the peptide segment in the acetylamino group restores the planarity and strengthens the π-conjugation, overcoming the steric hindrance of the two segments; (2) the enhancement of π-conjugation in the aniline (donor) segment increases the oscillator strength. This work demonstrates that INDO/S and AM1 calculations are of considerable value in elucidating the color-structure relationship for chromophoric systems with nonplanar geometries. The steric hindrance and an intramolecular hydrogen bond between donor and acceptor segments have been found to influence the absorption properties. Thus, the introduction of a suitable substituent, such as an acetylamino group, will cause a bathochromic shift with an increase in molecular extinction coefficient. These results afford a useful insight into the molecular design of new near-infrared dyes.

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Analysis of Solvent Effects on the Menshutkin Reaction

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Abstract: The reaction between ammonia and methyl bromide, which has been taken as a model for the Menshutkin reaction, has been studied through ab initio methods in the gas phase and in solution using discrete and continuum representations of the solvent. The solvent effect on this reaction bears a resemblance with other S_N2 reactions but also exhibits some differences with them. The main results turn out to be, on one hand, a decrease in the energy barrier upon increase in solvent polarity, and, on the other hand, the transition state is found earlier along the reaction coordinate, showing the participation of solvent parameters in the reaction coordinate. The polarization of the solute by the reaction field created by the solvent polarization is one of the most important aspects of the coupling between the solvent and the chemical system. This translates into an increase of the weight of the charge-transfer configuration with respect to the weight in the gas phase. Likewise, fluctuations increasing the reaction field are stabilized by instantaneous changes in the electronic distribution of the solute.

Introduction

One hundred years ago[1,2] Menshutkin published his landmark study about the solvent effect on the alkylation of tertiary amines by alkyl halides. Nowadays, in his honor, this reaction is known by his name. He found that the reaction rate increased dramatically with the polarity of the solvent employed, so he concluded that a reaction cannot be separated from the medium in which it is carried out. Unfortunately, the deep implications of this pioneering study of Menshutkin have not been taken into account for many years.

The Menshutkin reaction is a special kind of S_N2 reaction where the reactants are uncharged, in contrast to the most usual S_N2 reactions where one of the reactants is charged. In the last few years there has been an outgrowing number of theoretical papers dealing with the solvent effect on S_N2 reactions. For instance, the reaction of chloride with methyl chloride has received recently considerable attention.[3-21] From the analyses made so far on this particular reaction, the effects of solvent molecules have been classified into two main classes: static and dynamic.

The static effect of solvent molecules (also known as equilibrium effect) implies a separation between the chemical system and the bath. The solvent is equilibrated for each given geometry of the solute, so it plays a passive role in the chemical process. The bath makes only a different energetic contribution to the free energies of reactants and transition state, thus leading to a change in activation free energy and hence in the reaction rate.

Solvent effects which require a more dynamical treatment of solvent coordinates are called nonequilibrium or dynamic effects. The extent of equilibration of the solvent has been shown to be governed by the strength of the solute-solvent coupling, by the sharpness of the barrier, and by the characteristic time scale for the solute reaction motion. If the characteristic time scale for solvent reorganization is much slower than the time scale for solute reaction motion, nonequilibrium solvation effects on rate constants

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can be expected to be significant. This dynamic solvent effect translates, within the transition-state theory, into an important decrease of the transmission coefficient below unity. This decrease can be calculated either through the stochastic Langevin equation by means of a generalized friction force,[16] or through molecular dynamics by accounting for the trajectories that arise from reactants but recross the potential barrier induced by the solvent.[10,11] The dynamic solvent effect arises from the coupling of the reactant dynamics with fluctuations of the solvent, and ultimately from the direct participation of the solvent in the reaction coordinate.

Further consequences arise from the participation of the solvent in the reaction coordinate; the potential energy surface is modified and hence the position of stationary points. However, in symmetric processes like the reaction between chloride and methyl chloride, the position of the transition state is practically unchanged upon inclusion of solvent effects.[22] One of the most important aspects of solvent participation in the reaction coordinate is found in the coupling between the electronic structure of the solute and that of the solvent and vice versa, i.e., the electronic polarization of the solvent by the electronic distribution of the solute, and the feedback effect on the electronic structure of the solute by the reaction field. Attention to this last point has already been drawn in the case of S_N2 reactions by some authors.[12,14,18,23] This notwithstanding, electronic polarization of the solute is found to be unimportant in these studies.

The Menshutkin reaction and the chloride–methyl chloride reaction can be thought of as inner-sphere electron-transfer reactions. However, while the usual S_N2 reactions can be seen as a migration of charge, the Menshutkin reaction can be considered as a creation of two charges of opposite sign followed by its subsequent separation. This translates into an opposite effect of the solvent on these two types of reactions. Whereas usual S_N2 reactions are slowed down by the solvent, the Menshutkin reaction is favored by the presence of the solvent. Therefore, despite some common trends, solvent effects will be quite different in these two kinds of reactions. In particular, given that the Menshutkin reaction is not symmetric, one may expect an important modification in the position of the transition state in the potential energy hypersurface. Further, the polarization effect on the solute may be expected to be important because the ion-pair structures can be largely stabilized by the solvent.

The aim of the present paper is precisely to investigate the different aspects of solvent intervention on the Menshutkin reaction. Attention will be focused on the particular Menshutkin reaction between ammonia and methyl bromide:

$$NH_3 + CH_3Br \rightarrow NH_3CH_3^+ + Br^- \qquad (1)$$

where the solvent will be represented both by a continuum model and by a discrete model.

Methodology

The discrete representation for the solvent has been considered through the supermolecule approach, which severely limits the number of solvent molecules owing to practical limitations. Furthermore, the continuum representation has been taken into account through the SCRF model developed by Tomasi et al.,[24] where the solvent is represented by a continuous polarizable dielectric with permitivity ϵ. This continuum model, though not accounting for the specific interactions between the solvent and the solute (e.g., hydrogen bonds), in some way accounts for them because, in an equilibrium situation, the main component of specific interactions is electrostatic. In this method, the solute is placed inside a cavity accurately defined by its own geometry, whereas dielectric polarization due to the solute is simulated by the creation of a system of virtual charges on the cavity surface. This charge distribution on the surface polarizes in turn the charge distribution in the solute, this process being iterated until the solute electron density is self-consistent. The electrostatic contribution to the solvation free energy is obtained as the difference between the free energies computed with the continuum model and without it. Moreover, the cavitation free energy is calculated with Pierotti's equation.[25] The values required for the cavity model have been the same as those used in other studies of solvent effects.[26] The sphere radii used for atoms have been 20% larger than the van der Waals (or ionic) radii (hydrogen, 1.44 Å; carbon, 1.94 Å; nitrogen, 1.80 Å; bromide, 2.34 Å). All solvent effect calculations have been carried out at 298.15 K. For comparison purposes, we have also studied the effect of uniform electric fields. In this case, the one-electron Hamiltonian has been modified by the electron-field interaction term, and a fully relaxed electronic wave function solution has been always obtained.

Table I. Geometrical Parameters of Reaction 1 Computed with the 3-21G Basis Set[a]

species	d_{N-C}	d_{C-Br}	$\angle H_CCN$	$\angle H_NNC$
reactants	∞	2.000		
ion-pair reactant	3.153	2.011	72.6	107.1
transition state	1.883	2.605	97.0	108.9
ion-pair product	1.613	2.938	106.9	109.8
products	1.547	∞	107.7	110.7

[a] H_C and H_N stand for the hydrogen bonded to carbon and to nitrogen, respectively. Distances are given in Å, and angles in degrees.

Table II. Charges on the Most Important Fragments Present in Reaction 1, Dipole Moments of Stable Species, and Energies (kcal/mol) of the Stable Species Referred to Reactants Computed with Basis Set A (ΔE) and Basis Set B (ΔE^*)

species	Q_{Br}	Q_{CH_3}	Q_{NH_3}	μ	ΔE	ΔE^*
reactants	0.001	-0.001	0.000		0	0
ion-pair reactant	-0.058	0.042	0.016	4.8	-2.8	-3.2
transition state	-0.731	0.463	0.268	13.8	23.3	21.5
ion-pair product	-0.890	0.482	0.408	17.8	20.7	12.6
products	-1.000	0.483	0.517		103.8	84.9

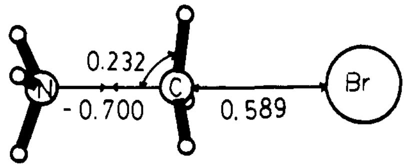

Figure 1. Optimized structure for the transition state of reaction 1, together with the main components of the transition vector.

Ab initio calculations have been used to compute the energy of the differential chemical systems appearing in this study. The size of the supermolecules and the models for the solvent compel restrictions in the basis set and level of calculation employed. Thus, we have used the 3-21G basis set[27,28] (hereafter named A) and the SCF level for all calculations. Nevertheless, we have carried out selected single-point calculations with another basis set (hereafter named B), where the bromide atom bears an additional diffuse sp function (α_{Br} = 0.0477) and the nitrogen and carbon atoms bear additional polarization d functions (α_N = 0.0864, α_C = 0.600). Geometry optimizations have been performed via commonplace gradient methods. The intrinsic reaction path (IRP)[29-31] has been computed with the GAMESS program[32] going downhill from the transition state in mass-weighted coordinates.[33,34] The IRP is followed taking successive very small steps in the direction of the negative gradient, which is equivalent to the Euler method. In this study we have

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Table III. Values of the Most Important Geometric Parameters, Reaction Coordinate R_c in the Gas Phase and in Solution, and Relative Energies Referred to Reactants, Also in the Gas Phase and in Solution, Computed with the 3-21G Basis Set for Reaction 1 and for the Discrete Representation of the Solvent[a]

species	d_{C-Br}	d_{C-N}	$R_{c_{solv}}$	$R_{c_{gas}}$	d_{N-O}	d_{Br-H}	ΔE_{solv}	ΔE_{gas}
reactants	2.000	∞	−∞	−∞	3.074	∞	0.0	0.0
ion-pair reactant	2.022	3.047	−1.025	−1.143	3.034	2.905	−5.0	−2.8
transition state	2.480	2.014	0.466	0.722	2.875	2.594	10.8	23.3
ion-pair product	3.032	1.564	1.468	1.325	2.696	2.485	−0.2	20.7
products	∞	1.529	∞	∞	2.566	2.464	59.2	103.8

[a] Distances are given in Å, and energies in kcal/mol.

also used the GAUSSIAN86[35] and MONSTERGAUSS[36] programs. The latter is used for calculations on the Tomasi model for the solvent.

Results

This section presents in the first place the results found for reaction 1 in the gas phase; then, the results for the discrete representation of the solvent are analyzed, and, finally, the results for the continuum model of the solvent are reported.

Gas-Phase Results. We summarize in Table I the main geometrical parameters of the gas-phase stationary points of reaction 1 optimized with the 3-21G basis set, for which we present in Table II the charges, dipole moments, and energies related to reactants computed with basis sets A and B. Observation of Table I shows clearly that the methyl group is being transferred from bromine to ammonia, together with the typical umbrella inversion about the carbon atom. The main three geometrical parameters involved in the methyl transfer are also those most significant in the transition vector of the reaction, which is depicted in Figure 1. It is interesting to note that the carbon–bromine bond is fairly broken and that the umbrella has already been inverted in this transition state, so the transition state is found quite late along the reaction coordinate. 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_{C-Br} and R_{N-C}; 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.

Turning attention to Table II, one can see that the negative charge on bromine increases along the reaction coordinate until it reaches unity. On the contrary, an opposite positive charge appears on methyl and ammonia spread over both fragments. In the early stages of the reaction, the positive charge is more localized on the methyl group, but it spreads over nitrogen as the system evolves toward the final products. This charge separation translates into a large dipole moment which is especially large after the transition state. This emerging dipole moment will obviously cause a huge stabilization by interaction with polar solvents. In the two rightmost columns of Table II we have collected the energies of stationary points related to separated reactants computed with basis sets A and B. The corresponding energy profile computed with basis set A is depicted in Figure 2. One can see that this reaction exhibits a double-well energy profile like all S_N2 reactions; however, its shape is very asymmetric, and the transition state is found late along the reaction coordinate. The effect of the additional basis functions of basis set B is to lower the potential barrier of the reaction, to increase the well depth of the second ion-pair intermediate, and to increase the well depth of the first ion-pair intermediate, yet to a smaller extent than the second one. In previous calculations using the semiempirical MNDO method of a particular Menshutkin reaction between pyridine and methyl chloride,[37] the double-well energy profile typical of S_N2 reactions was not found. Thus, the general effect of the increase in basis set is to improve the double-well character of the energy profile. With both basis sets used in the present work, a highly endothermic process is obtained, which agrees with the fact that no Menshutkin reaction has ever been reported in the gas phase.[38]

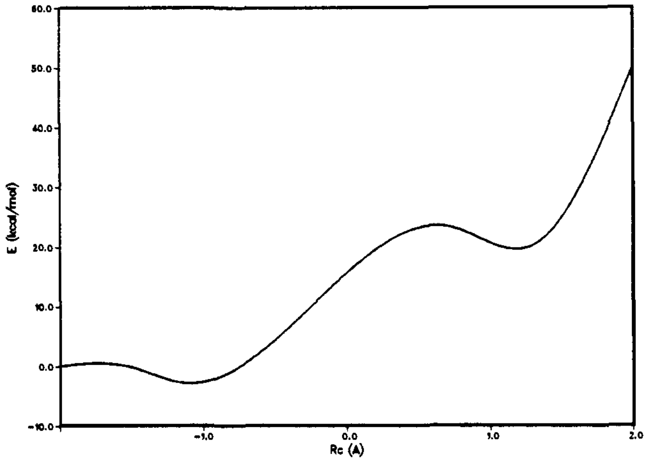

Figure 2. Energy profile for reaction 1 in the gas phase computed with the 3-21G basis set.

Discrete Representation of the Solvent. As mentioned in the Methodology section, in the supermolecule model for the solvent practical restrictions limit the number of solvating molecules. In this study, we have considered two water molecules, one solvating bromine and another solvating ammonia. The water molecule is not hydrogen-bonded to any 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–Br axis, interacting simultaneously with all three hydrogens of ammonia. This geometrical arrangement prevents breaking artifically the symmetry of the reaction.

We collect in Table III the most important geometric parameters, the values of the reaction coordinate, and the energies relative to reactants for reaction 1 in the gas phase and with the inclusion of two water molecules. From the values of this table, it is shown that the transition state is found earlier along the reaction coordinate when two water molecules are considered. On the contrary, the first and second intermediates are found later in the reaction coordinate with respect to the gas phase. Paying attention to relative energies, one can see that, with respect to the gas phase, the energy stabilization is larger the more advanced the reaction coordinate is. This stabilization is especially important in the second intermediate and in the separated products. This fact is due to two main reasons: first, the two emerging charges are stabilized by the solvent; second, the emerging charges are delocalized over the respective solvating water molecules. The global effect of the inclusion of the two water molecules is 2-fold: first, there is a decrease in energy barrier; second, the transition state is found earlier along the reaction coordinate. This effect can be foreseen given that the endothermicity of the process is decreased.

As to solvent parameters, the N–O and Br–H distances shorten with the advance of the reaction, so there is a contraction of the solvation shell around both fragments. This fact is completely

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Table IV. Bond Lengths of the Most Important Geometric Parameters, Reaction Coordinate R_c, Charges Q on Bromide, Methyl, and Ammonia Groups, Dipole Moments (μ_T), and Relative Energies of the Stable Species Referred to Reactants Computed with Basis Set A (ΔE) and Basis Set B (ΔE^*) for Reaction 1 and for the Continuum Representation of the Solvent[a]

species	$d_{C\text{-}Br}$	$d_{C\text{-}N}$	R_c	Q_{Br}	Q_{CH_3}	Q_{NH_3}	μ_T	ΔE	ΔE^*
				$\epsilon = 1.88$					
reactants	2.000	∞	−∞	−0.0232	0.0232	0.0		0.0	0.0
ion-pair reactant	2.011	3.154	−1.143	−0.0786	0.0615	0.0171	5.0	−1.6	−2.2
transition state	2.488	2.034	0.454	−0.6710	0.4593	0.2117	12.6	12.8	14.5
				(−0.6004)	(0.4181)	(0.1823)	(11.5)		
ion-pair product	3.131	1.602	1.529	−0.9399	0.4792	0.4608	19.7	3.0	−5.7
products	∞	1.547	∞	−1.0000	0.4714	0.5286		41.6	23.6
				$\epsilon = 32.66$					
reactants	2.000	∞	−∞	−0.0592	0.0592	0.0		0.0	0.0
transition state	2.356	2.200	0.157	−0.5906	0.4378	0.1528	11.2	8.5	8.5
				(−0.4440)	(0.3353)	(0.2207)	(9.0)		
products	∞	1.547	∞	−1.0000	0.4531	0.5469		−24.6	−41.6
				$\epsilon = 78.36$					
reactants	2.000	∞	−∞	−0.0586	0.0586	0.0		0.0	0.0
transition state	2.356	2.200	0.157	−0.5909	0.4372	0.1536	11.2	8.1	8.3
				(−0.4440)	(0.3353)	(0.2207)	(9.0)		
products	∞	1.547	∞	−1.0000	0.4536	0.5464		−27.0	−44.0

[a] Values in parentheses have been obtained in the gas phase. Distances are given in Å, charges in atomic units, energies in kcal/mol, and dipole moments in debyes.

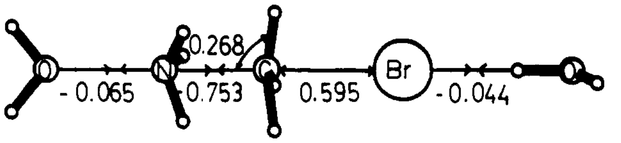

Figure 3. Optimized structure for the transition state of reaction 1 in the discrete representation of the solvent, together with the main components of the transition vector computed with the 3-21G basis set.

opposite to what happens in typical S_N2 charge-migration reactions, where one solvent shell is contracted and another one is expanded. In reaction 1 two charges of opposite sign are created, so both shells are contracted. The noticeable participation of the solvent parameters in the reaction coordinate is also shown in the corresponding components of the transition vector depicted in Figure 3. Besides the typical components corresponding to the N–C and C–Br distances and to the umbrella inversion, the components corresponding to the two solvent distances have meaningful values, so it is clear again that solvent parameters belong to the reaction coordinate. Therefore, the discrete representation of the solvent with a reduced number of solvent molecules, though not allowing for the bulk reorganization, is especially suited to show the participation of solvent parameters in the reaction coordinate. As a matter of fact, a similar model has been used in a symmetric S_N2 reaction to discuss the extent of nonequilibrium solvation by comparing calculations in which the water molecule degrees of freedom participate in the reaction coordinate to those in which they do not.[20]

Continuum Representation of the Solvent. The continuum model described in the Methodology section has been applied to reactants, products, and the first ion-pair intermediate at their gas-phase optimized geometry. However, since we are interested in the displacements of the transition state and later stationary points along the reaction coordinate, we have applied the continuum model along selected points of the intrinsic reaction path (IRP). This IRP has been built starting from the transition state toward the first intermediate, and from products toward the second intermediate. In this way, new potential energy profiles have been obtained, by adding the free energy of solvation to the internal geometry of the solute.

In Table IV we collect the geometrical parameters, charges, relative energies, and dipole moments for the different stationary points for three selected solvents (*n*-hexane, $\epsilon = 1.88$; methanol, $\epsilon = 32.66$; and water, $\epsilon = 78.36$). If we focus on the value of the reaction coordinate and compare it with the gas-phase values of Table I, we notice that for *n*-hexane the transition state is found earlier along the reaction coordinate, whereas the second intermediate is found late. More striking results are obtained for methanol and water, for which the transition state is found even earlier, there is no second intermediate because the solvent stabilization leads to a continuous decrease in energy toward separated ions, and the first intermediate also disappears, the profile thus becoming unimodal.

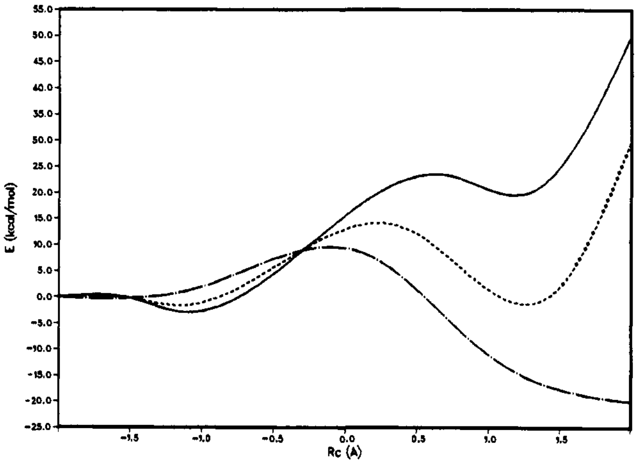

Figure 4. Energy profiles for reaction 1. Continuous line, dotted line, and dash-dotted line represent the energy profiles in the gas phase, *n*-hexane, and water, respectively.

The evolution of the position of the different stationary points along the reaction coordinate, together with their energies, are represented in Figure 4 for *n*-hexane, water, and the gas phase. From Table IV and Figure 4 it emerges that the position of the transition state, which is found earlier the larger the dielectric constant of the solvent, is associated to a decrease in the potential energy barrier of the process. These energy profiles agree qualitatively with experience: in opposition to its behavior in the gas phase, the Menshutkin reaction proceeds with all three solvents, the faster the larger the dielectric constant. Further, when methanol or water is used as solvent, the separated solvated ions are found as products; however, when the reaction is carried out in *n*-hexane, a crystalline salt product is obtained.

As mentioned in the Introduction, one of the goals of the present paper is to address the coupling between the electronic structure of the solute and that of the solvent. When water is considered in the continuum model, one not only considers the instantaneous polarization of the electronic cloud of the solvent, but also incorporates the polarization due to reorientation of solvent molecules. Any frozen solvent model should affect only polarization by reorientation, but not electronic polarization because it is almost instantaneous. The electric polarization may be represented by

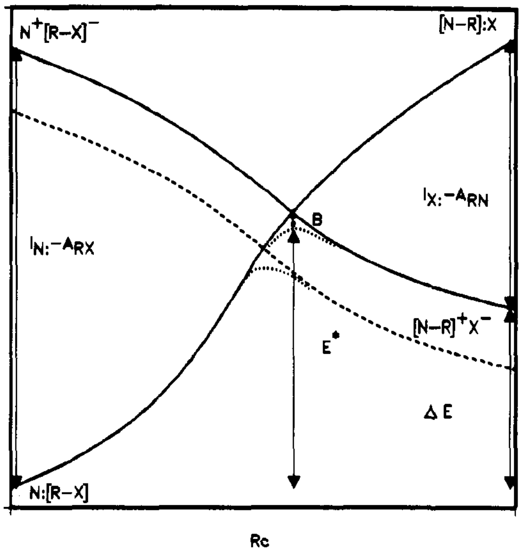

Figure 5. State correlation diagram for a Menshutkin reaction.

the so-called optical dielectric constant (ca. $\epsilon = 2$). Thus, comparison of profiles for $\epsilon = 78.36$ and $\epsilon = 1.88$ provides an indication of the change in energy arising from the frozen solvent referred exclusively to the polarization by reorientation. However, the most important aspect is the feedback effect, that is, the polarization of the solute due to the reaction field created by the polarization of the solvent. A deeper insight into this aspect may be obtained by looking at the charges and dipole moments for the different stationary points in solution (Tables II and IV). In addition, for transition states the charges and dipole moments corresponding to identical geometries computed in the gas phase are also shown. In general, the dipole moments of transition states are quite larger in solution than in the gas phase, owing to the polarization of the solute by the reaction field. Paying attention to water, one can see that the negative charge on bromine increases from 0.44 to 0.59 from the gas phase to solution, whereas the positive charge on the CH_3NH_3 group increases to the same extent. From an electronic point of view, given that the reaction consists of a continuous charge separation, the polarization effect is equivalent to an advance in the reaction coordinate. The same effect could have been obtained by advancing in the reaction coordinate defined by geometrical parameters. Therefore, it is shown that the reaction field created by the solvent belongs to the correct definition of the reaction coordinate, which is understood in a wider sense than usual. This evidences one of the most important aspects of the participation of solvent in the reaction coordinate.

Discussion

The main results obtained in the present study of the solvent effect on the Menshutkin reaction are a decrease in endothermicity and, in agreement with the Hammond principle, an earlier transition state in the reaction coordinate and a lowering of the energy barrier. However, the change in the electronic structure of the transition state is not parallel to an identical change in the geometrical structure, because the polarization due to the reaction field acts in an opposite way to the geometric change, the former compensating the latter to some extent. In order to understand this special aspect of the Menshutkin reaction, we present in Figure 5 the state correlation diagram model for this process, which is similar to that constructed by Shaik for a general S_N2 reaction.[8] With respect to the diagram for an S_N2 reaction involving anionic reactants, the main change is that the ionization potential is much larger for a neutral nucleophile than for a charged nucleophile, so the gap between the two quasidiabatic curves is much larger at reactants for the Menshutkin reaction. Another important change is that the Menshutkin reaction is endothermic. The equation for the activation energy for this diagram model is given by

$$E^* = f(I_N - A_{RX}) - B \qquad (2)$$

where f depends, among other factors, on the endothermicity of the process. Therefore, E^* is larger for the Menshutkin reaction than for a typical S_N2 reaction because (a) $I_N - A_{RX}$ is larger, and (b) the f factor increases owing to the endothermicity. Since the reaction is endothermic and the transition state is found late in the reaction coordinate, one can understand that a large energy barrier is found for this process, since the R–X bond is broken more at the transition state than in normal S_N2 reactions. The most noticeable difference between the Menshutkin reaction and a typical S_N2 reaction lies in the difference between the quasidiabatic curves. Whereas for a typical S_N2 reaction both the quasidiabatic curve corresponding to reactants and that corresponding to products are charged, for the Menshutkin reaction the quasidiabatic curve for reactants is neutral, while that for products corresponds to an ion pair, so for the Menshutkin reaction the solvent will stabilize the quasidiabatic curve of products but not that of reactants. Therefore, the effect of a polar solvent on the Menshutkin reaction (Figure 5) will be to position the transition state earlier in the reaction coordinate, to lower the energy barrier, and to decrease the endothermicity of the process. However, the electronic structures of the transition state in the gas phase and in solution will be similar because they arise from avoided crossings corresponding to quasidiabatic curves of the same nature.

For a given point along the reaction coordinate, the stabilization of the ion-pair configuration (quasidiabatic curve of products) by effect of the solvent increases the weight of that configuration in the adiabatic wave function. Therefore, the wave function in solution is very different from that in the gas phase, thus explaining the results obtained in our study regarding the polarization of the solute by the reaction field.

These results shed light on important aspects of the usual method of estimating the dipole moment of transition states, μ^*. In general, use is made of Kirkwood's equation[39-42] as incorporated into transition-state theory:

$$\Delta G^*_{S_1 \to S_2} = \frac{-\mu^*}{2a}[f(\epsilon_2) - f(\epsilon_1)] \qquad (3)$$

where $\Delta G^*_{S_1 \to S_2}$ is the change in the activation free energy of the reaction associated to the change from solvent 1 and 2, **a** is the radius of the spherical cavity in whose center $\vec{\mu}$ is embedded, and $f(\epsilon)$ is a dielectric function as defined in reaction field theory.

It is implicitly accepted that μ^* is independent of the solvent.[38,43,44] Our results show that the dipole moment of the transition state does not change very much as compared to geometrical changes. Thus, in the experimental work carried out with solvents of similar ϵ, considering μ^* constant should be a good approximation and thus would rationalize the success of eq 3. This point is also of fundamental importance when considering the use of transfer functions for transition states,[45,46] for which the basic underlying hypothesis is again that of a constant value for μ^*.

The main conclusion of our study using the discrete representation for the solvent is that solvent parameters belong to the reaction coordinate. Thus, one may think that the solvent plays a much more active role than usually thought. Whereas solvent reorganization may be considered to follow the chemical process, the opposite view may be also considered: the chemical process can be induced by solvent fluctuations.

A recent dynamical study on the S_N2 reaction shows that the reorganization of the solvent to a state appropriate to solvating

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Table V. Bond Lengths of the Most Important Geometric Parameters, Reaction Coordinate R_c, Charges Q on Bromide, Methyl, and Ammonia Groups, Relative Energies Referred to Reactants, and Dipole Moments (μ_T) Computed with the 3-21G Basis Set for Reaction 1 and for the Different Electric Fields Applied[a]

species	d_{C-Br}	d_{C-N}	R_c	Q_{Br}	Q_{CH_3}	Q_{NH_3}	μ_T	ΔE
				EF = 0.005				
reactants	2.010	∞	−∞	−0.0529	0.0529	0.0		0.0
ion-pair reactant	2.029	3.058	−1.029	−0.1254	0.1028	0.0226	5.6	−3.8
transition state	2.516	2.007	0.509	−0.6832	0.4584	0.2248	12.9	12.0
				(−0.6325)	(0.4344)	(0.1981)	(12.0)	
ion-pair product	3.083	1.584	1.499	−0.9263	0.4819	0.4444	19.2	3.0
products	∞	1.559	∞	−1.0000	0.5024	0.4976		12.5
				EF = 0.01				
reactants	2.024	∞	−∞	−0.1089	0.1089	0.0		0.0
ion-pair reactant	2.055	2.955	−0.900	−0.2023	0.1703	0.0320	6.5	−5.3
transition state 1	2.436	2.139	0.296	−0.6370	0.4513	0.1859	12.2	2.7
				(−0.5296)	(0.3913)	(0.1383)	(10.4)	
ion-pair product	3.303	1.566	1.741	−0.9550	0.4767	0.4787	20.9	−15.5
transition state 2	4.490	1.551	2.939	−0.9770	0.4823	0.5150	27.5	−12.4
				(−0.9955)	(0.5220)	(0.4735)	(27.0)	
products	∞	1.559	∞	−1.0000	0.5217	0.4783		−48.4

[a] Values in parentheses have been obtained in the gas phase. Distances are given in Å, charges in atomic units, energies in kcal/mol, and dipole moments in debyes.

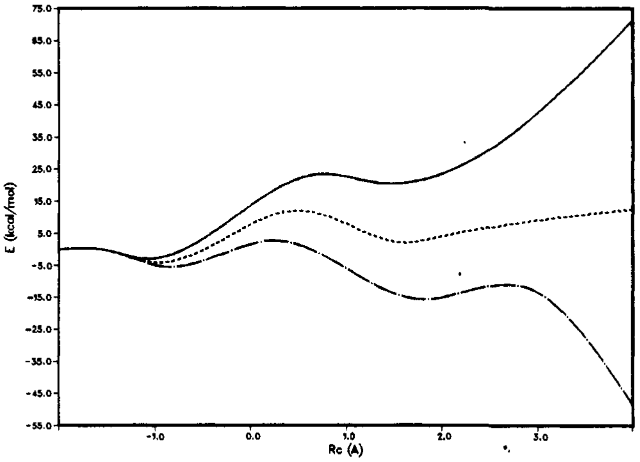

Figure 6. Energy profiles for reaction 1 in presence of electric fields. Continuous line, dotted line, and dash-dotted line represent the energy profiles in the free system and in the presence of electric fields of intensity 0.005 and 0.01 au, respectively.

the reactants at the barrier top takes place well before the charge distributions on the reactants begins to take place.[21] According to Warshel's nomenclature,[14] this is a solvent-driven process. One may question if in this Menshutkin reaction the solvent fluctuations precede the chemical reaction; i.e., it is solvent-driven or, on the contrary, it is solute-driven. Although the correct answer should be found through molecular dynamics techniques, an indirect answer can be found by applying uniform electric fields to reaction 1 in the gas phase. For that purpose, we present in Figure 6 the potential energy profiles for reaction 1 under two different intensities of a uniform electric field. The overall effects turn out to be similar to those found in Figure 4 for solvent effects: with the increase in intensity of the electric field, the transition state is found earlier in the reaction coordinate, the potential energy barrier is lowered, and the reaction becomes exothermic. One difference arises in that a second transition state is found for high fields (EF = 0.01 au). The reason for this difference may be found in the fact that, whereas for the solvated reaction the reaction field increases along the reaction coordinate, for uniform electric fields the intensity is constant all along the reaction. It must be remarked that the chemical system aligns spontaneously with the electric field for the reaction to proceed. In Table V we collect the geometrical parameters, charges on fragments, relative energies, and dipole moments for the stationary points of reaction 1 influenced by electric fields of intensities 0.005 and 0.01 au. By comparison with Table II, one can see that the effects of electric fields are similar to those of solvents. It is especially interesting to look at the values of charges on fragments and dipole moments at the geometries of the transition states under the applied electric fields and in the gas phase. It is found that electric fields increase the separation of charge, and hence the dipole moments, so again it is evidenced that the uniform electric field belongs to the reaction coordinate. Turning our attention to the effects of solvent fluctuations, appropriate fluctuations of the solvent in such a way to contract the solvation shells around the two emerging ions of different sign would have an effect similar to creating an electric field like those considered in this section. These solvent fluctuations would advance the reaction from an electronic point of view, and the polarized solute would in turn stabilize those solvent fluctuations, hence ensuring their kinetic success.

Conclusions

The Menshutkin reaction is an S_N2 reaction which differs from other processes of this kind in that there is no charge migration, but rather there is a charge separation. This difference translates into an opposite effect of the solvent. While for typical S_N2 reactions polar solvents decrease the reaction rate, for the Menshutkin reaction the reaction rate is increased. This difference arises from the different static effects of the solvent: whereas for typical S_N2 reactions the charge in the transition state is quite delocalized, so it is less stabilized by solvents than reactants; for the Menshutkin reaction the charge separation increases along with the advance of the reaction, so there is a progressive stabilization of the chemical system. This charge separation brings about a noticeable solvent reorganization, so a frozen model for the solvent about the crossing of the top of the barrier will have a negative effect on the rate of the Menshutkin reaction, as happens with typical S_N2 reactions.

The Menshutkin reaction carries further differences with respect to other S_N2 reactions. Because of the solvent intervention in the reaction coordinate, an earlier transition state is found along the reaction coordinate. This advance is found even when the continuum model for the solvent is used, i.e., when the solvent is in equilibrium with the solute at all points along the reaction coordinate. One of the most important aspects of this intervention of the solvent is the polarization of the solute due to the reaction field. This field leads to an electron distribution which represents, from an electronic point of view, an advance in the reaction coordinate with respect to the gas phase. The polarization of the solute arises from an increase in the weight of the charge-transfer configuration in the electronic wave function. The coupling between the reaction field and the solute polarization is very important in understanding the dynamic coupling between the solvent and the chemical system. The reaction field stands for a mean value, and instantaneous fluctuations increasing the field originate a solute polarization which in turn stabilizes noticeably the solvent fluctuations, which will cause an electronic advance along the reaction coordinate. In turn, this electronic advance will augment the probability of these fluctuations and guarantee their kinetic success.

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Molecular Hydrogen Complexes with a Hydride Ligand. An ab Initio Study on the $[Fe(PR_3)_4H(H_2)]^+$ System[†]

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Abstract: Specific effects of the hydride ligand in the coordination of the hydrogen molecule to metallic centers are studied by means of ab initio MO calculations in the model system $[Fe(PH_3)_4H(H_2)]^+$. The two different isomers of this complex (cis and trans) are optimized, several orientations of the hydrogen molecule being considered for the cis isomer. In contrast to phosphine, the hydride ligand favors the coordination of hydrogen to the metal both in the cis and trans positions. When the hydride is placed in the cis position and oriented suitably, there is a strong attractive effect between it and the molecular hydrogen. Discussion of the obtained results is carried out in comparison with the available experimental data.

Introduction

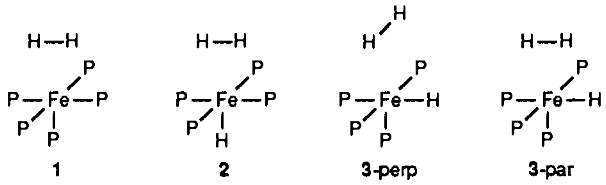
After their discovery in the mid-eighties,[1] molecular hydrogen complexes have come a long way. Nowadays, nonoxidative coordination of molecular hydrogen to metallic centers is quite common, as shown in the growing number of reviews[2] reflecting the large scientific activity[3] developed on this subject. From being initially a scientific oddity, namely, feasible intermediates in certain chemical reactions, molecular hydrogen complexes have become compounds of definite stability whose specific chemical reactivity is the subject of an increasing number of studies.

One of the most interesting subgroups of molecular hydrogen complexes is constituted by those where the H_2 ligand coexists with the hydride ligand. Besides the curiosity arising from any chemical species reported so recently, the possible interchange of a hydrogen atom between hydride and H_2 makes the molecular hydrogen–hydride complexes the simplest model for the very general class of heterolytic activation reactions[4] (also referred to in the literature as σ-bond metathesis[5a] and tetracentric mechanism activations).[5b]

The experimental study of molecular hydrogen–hydride complexes is made more difficult by the problems inherent to the identification of the molecular hydrogen ligand. These problems turn out to be especially important when yet more hydrogens are involved as ligands. The only method allowing for their unequivocal identification is neutron diffraction. However, this method requires the existence of fairly large crystals, so the amount of available data is still scarce.[1,6,7] Although other techniques like X-ray diffraction[1,8] and IR[9] or NMR[10] spectroscopy have been also applied, they have not found universal application.

Among the complexes that could be considered as candidates to contain simultaneously molecular hydrogen and hydride as ligands, mention can be made of the following complexes: $[Ir(bq)(PR_3)_2H(H_2)]^+$,[11a] $[Fe(R_2PCH_2CH_2PR_2)_2H(H_2)]^+$,[6,11b] $[Fe(P(OEt)_3)_4H(H_2)]^+$,[11c] $[Fe(P(CH_2CH_2PR_3)_3)H_3]^+$,[11d,e] $[Fe[PR_3)_3H_2(H_2)]^+$,[7] $[Ru(Cp)(PR_3)H_3]$,[11f] and $[Ir(Cp)(PR_3)H_3]^+$.[11g] All complexes in this list have the formal structure d^6 $ML_5(H_2)$, which otherwise is quite common among molecular hydrogen complexes. It is worth remarking the relative abundance of data for iron complexes having the metal coordinated to four PR_3 groups, one hydrogen molecule, and one hydride; one of them is

Scheme I



trans-$[Fe(R_2PCH_2CH_2PR_2)_2H(H_2)]^+$, perhaps one of the best known molecular hydrogen complexes. For this species, the

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[†] A contribution from the "Grup de Quimica Quântica de l'Institut d'Estudis Catalans".

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