

APPLICATION OF SOLVATON MODEL  
TO QUANTUM-CHEMICAL STUDY OF INFLUENCE OF SOLVATION  
ON THE CHEMICAL PROCESS  $\text{NH}_3 + \text{HF} \rightarrow \text{NH}_4^+ + \text{F}^-$

Stanislav MIERTUŠ and Josef BARTOŠ

*Institute of Polymers,  
Slovak Academy of Sciences, 809 34 Bratislava*

Received February 19th, 1979

Influence of solvent ( $\text{H}_2\text{O}$ ) on the system  $\text{NH}_3 + \text{HF} \rightarrow \text{NH}_4^+ + \text{F}^-$  has been studied with the use of the solvaton model at the level of the semiempirical CNDO/2 method. The solvent has been found to cause changes in equilibrium geometries and charge distributions particularly in the polar components of the system. Hydration stabilizes much more the charged components, hence the reaction equilibrium should be shifted to the right in aqueous medium. Hydration also facilitates the proton-transfer from HF to  $\text{NH}_3$ , and the ion pair  $\text{H}_3\text{NH}^+ \cdots \text{F}^-$  should be the most stable intermediate in aqueous medium according to the calculations.

In the last period quantum chemists are increasingly interested in interpretation of solvent effects on properties of solute molecules<sup>1,2</sup>. This trend can be understood, since most chemical processes proceed in liquid phase. It still remains doubtful which of the quantum-chemical approaches describes with sufficient reliability the influence of solvent molecules on solute molecules. With respect to exactness the so called supermolecule model seems to be the most suitable: it considers the solvent to be a discrete set of molecules surrounding the solute molecule: the calculation is carried out for the whole supermolecule. Here it is necessary to optimize the position of the solvent molecules relative to the solute molecule, sometimes being insufficient to consider the first solvation sphere only. High computer time requirements and problems of the choice and location of the solvent molecules prevent this model to be more widely used particularly in its application to larger molecules. Another possibility of involvement of solvent effect on change of properties of the solute molecule is represented by the approximative approaches characterizing the solvent either as a set of point charges or as a dielectric continuum. These models need considerably lower computer time as compared with the former model. On the other hand, however, we face a problem to what extent the approximative character of the models weakens their predictive power as compared with the supermolecular solvaton model.

This communication deals with study of influence of solvent ( $\text{H}_2\text{O}$ ) on system  $\text{NH}_3 + \text{HF} \rightarrow \text{NH}_4^+ + \text{F}^-$ . This problem was investigated by Kollmann and Kuntz<sup>3</sup> and Neoll and Morokuma<sup>4</sup> using the supermolecular model at the *ab initio* level. For our study of this problem we used the solvaton model<sup>5,6</sup> which was relatively successful in quantitative investigation of solvent effects on UV and ESR spectra of conjugated molecules.

## METHOD OF CALCULATIONS

The solvaton model<sup>5,6</sup> represents solvent as induced point charges, called solvatons, in the surroundings of solute molecule. One solvaton charge  $Q_s$  corresponds to each atomic centre of the molecule. The Hamiltonian of the molecule having  $N$  valence electrons and  $M$  atomic cores with charges  $Z_m^c$  and dissolved in a solvent with relative permittivity  $\epsilon_r$  has the following form:

$$\mathbf{H} = \mathbf{H}_0 - \left[ \sum_{\mu'=1}^N \sum_{s'=1}^M \frac{Q_{s'} e^2}{4\pi\epsilon_0 r_{\mu's'}} - \sum_{m=1}^M \sum_{s'=1}^M \frac{Z_m^c Q_{s'} e^2}{4\pi\epsilon_0 r_{ms'}} \right] \quad (1)$$

As the solvaton's charges are considered proportional to the corresponding charges at atomic centres of the solute molecule

$$Q_{s'} = -(1/2)(1 - 1/\epsilon_r) Q_s, \quad (2)$$

the overall interaction will be determined by the charges  $Q_s$  on the solute molecule and by relative permittivity  $\epsilon_r$  of the solvent. Details of the original and the modified solvaton model are given in refs<sup>5-7</sup> within the framework of the CNDO/2 version.

Total energy of the solute-solvent interaction involves the electrostatic-coulombic and the polarization contributions. The former term itself can be expressed (within this model), using the perturbation theory, by the equation derived by Jano<sup>8</sup>:

$$E_{\text{solv}}^{\text{e1-coul}} = -\frac{1}{2} \left( 1 - \frac{1}{\epsilon_r} \right) \sum_A^M \sum_B^M Q_A Q_B \gamma_{AB}, \quad (3)$$

where  $Q_A$  and  $Q_B$  are pure charges at the atoms A and B, respectively,  $\gamma_{AB}$  is the bicentric two-electron integral, which makes it possible to compare, within the framework of the solvaton model of solvation, relative contributions of the coulombic and the polarization terms to the total solvation energy.

The calculations were carried out by the standard CNDO/2, method<sup>9</sup>. The solvent ( $\text{H}_2\text{O}$ ) was characterized by relative permittivity  $\epsilon_r = 80$ .

## RESULTS AND DISCUSSION

The study of hydration of the system  $\text{NH}_3 + \text{HF} \rightarrow \text{NH}_4^+ + \text{F}^-$  was divided into three parts: A) calculation of hydration energies of the individual components of the system ( $\text{NH}_3$ ,  $\text{HF}$ ,  $\text{NH}_4^+$ ,  $\text{F}^-$ ) and investigation of the solvent effect on the equilibrium geometries and charge distributions in these components, B) solvent effect

on the reaction enthalpy of the mentioned process, and C) solvent effect on the reaction course involving the intermediate stages:  $\text{NH}_3 + \text{HF} \rightarrow \text{H}_3\text{N}\cdots\text{HF} \rightarrow \text{H}_3\text{NH}^+\cdots\text{F}^- \rightarrow \text{NH}_4^+ + \text{F}^-$ .

*Effect of Solvent on Physico-Chemical Properties of Components of the System  $\text{NH}_3\text{-HF}$*

The equilibrium geometries of the components in gas phase calculated by the CNDO/2 method were taken from ref.<sup>9</sup>. The geometries of the components in aqueous phase were optimized by minimization of the total energy, the bond lengths being considered only for simplicity. The results given in Table I indicate that the polar bond in HF (aq) is lengthened in the strongly polar solvent. Involvement of solvent effect results in change of electron distribution in all polyatomic systems, leading to a change in the bond polarity. The change becomes greater with the increasing difference of electronegativities of the bonded atoms. Difference between the total energy for  $\epsilon_r = 80$  and that for  $\epsilon_r = 1$  provides the hydration energy of the individual components. Table I also gives the values of the coulombic contribution to the total hydration energy calculated from the Jano equation (3). From these values it follows that, whereas the total hydration energy of the charged components  $\text{F}^-$  and  $\text{NH}_4^+$  has pure electrostatic-coulombic nature (the polarization term of  $\text{NH}_4^+$  is negligible due to its symmetry), with the neutral molecules  $\text{NH}_3$  and HF the polarization contribution makes about 45% of the total hydration energy. This calculation suggests that general use of the Jano relation – especially in the situation accompanied by change of the overall charge – can lead to incorrect conclusions.

Comparison of the calculated hydration energies with the experimental ones shows good agreement for slightly polar ( $\text{NH}_3$ ) and, partially, also for strongly polar molecules (HF). In the case of the ionic components  $\text{NH}_4^+$  and  $\text{F}^-$  the hydration energies are overestimated.

The problem of hydration of  $\text{NH}_4^+$  and  $\text{F}^-$  was treated by the supermolecular approach at the *ab initio* level<sup>3</sup>. The calculations give the value for hydration energy of  $-348.34 \text{ kJ mol}^{-1}$  for hydration of  $\text{NH}_4^+$  by the first hydration sphere consisting of 4 water molecules, the stabilization being increased by further  $70 \text{ kJ mol}^{-1}$  on addition of the second sphere. Similar calculation gives the values  $-569.82 \text{ kJ mol}^{-1}$  in the case of  $\text{F}^-$ . In the both cases the supermolecular model also provides higher hydration energy values, which are, however, nearer to the experimental data than those of the solvaton model used by us. Nevertheless, there exist also such cases (*e.g.* hydration of  $\text{Li}^+$ ) where this very supermolecular model<sup>3</sup> exceeds the experimental value much more than the solvaton model<sup>13</sup>. On the other hand, there are no published calculations yet giving the hydration energies of  $\text{NH}_3$  and HF by the supermolecular approach, where it is the solvaton model which gives satisfactory agreement.

TABLE I  
Equilibrium Geometries<sup>a</sup>, Charge Distributions, Calculated and Measured Hydration Energies<sup>b</sup> of Components of the System  $\text{NH}_3 + \text{HF} \rightarrow \text{NH}_4^+ + \text{F}^-$

Com- ponent	$\epsilon_r = 1$						$\epsilon_r = 80$						$\Delta H_{\text{sol}}^{\text{exp}}$	
	$r$	$Q_N$	$Q_H$	$Q_F$	$r$	$Q_N$	$Q_H$	$Q_F$	$r$	$Q_N$	$Q_H$	$Q_F$		$E_{\text{sol}}^{\text{cal}}$
$\text{NH}_3$	1.07	-0.224	+0.074	-	1.07	-0.328	+0.109	-	-	-29.4	-15.9	-34.7 <sup>c</sup>	-15.9	-34.7 <sup>c</sup>
$\text{HF}$	1.00	-	+0.266	-0.266	1.02	-	-0.336	+0.336	-	-86.4	-47.1 <sup>c</sup>	-34.7 <sup>c</sup>	-47.1 <sup>c</sup>	-34.7 <sup>c</sup>
$\text{NH}_4^+$	1.07	-0.086	+0.272	-	1.07	-0.035	+0.259	-	-	-530.7	-528.0	-303.7 <sup>d</sup>	-528.0	-303.7 <sup>d</sup>
$\text{F}^-$	-	-	-	-1.000	-	-	-	-1.000	-	-1.226.3	-1.226.3	-502.4 <sup>c</sup>	-1.226.3	-502.4 <sup>c</sup>

<sup>a</sup> Interatomic distances in  $10^{-10}$  m; <sup>b</sup> hydration energies in  $\text{kJ mol}^{-1}$ ; <sup>c</sup> ref.<sup>10</sup>; <sup>d</sup> ref.<sup>11</sup>; <sup>e</sup> ref.<sup>12</sup>.

*Solvent Effect on Reaction Enthalpy of Reaction  $\text{NH}_3 + \text{HF} \rightarrow \text{NH}_4^+ + \text{F}^-$*

Knowing the total energies of components of the studied chemical system, it is possible to calculate the difference between the initial and the final states and compare it with the experimental reaction enthalpy. The calculation indicates that the reaction is endothermic in gas phase ( $\Delta E = +1243.7 \text{ kJ mol}^{-1}$ ), and the equilibrium will be shifted in favour of the starting components, if the entropy effect is neglected. On involvement of the solvent effect the situation is reversed: the reaction is exothermic ( $\Delta E = -397.4 \text{ kJ mol}^{-1}$ ). Comparison of the latter value with the experimental reaction enthalpy in aqueous medium ( $\Delta H_{\text{exp}} = -77.8 \text{ kJ mol}^{-1}$ ) reveals qualitative agreement. The higher calculated value is obviously due to that the solvaton model overestimates the hydration of  $\text{F}^-$  and  $\text{NH}_4^+$ . From the calculated reaction enthalpy it follows that the equilibrium should be shifted in favour of formation of the ions. However, at the same time it must be noted that the entropy effect, which is due to the more regular arrangement of the solvent molecules in the surroundings of ions, can shift the equilibrium in favour of the starting neutral components.

*Solvent Effect on the Reaction Course  $\text{NH}_3 + \text{HF} \rightarrow \text{NH}_4^+ + \text{F}^-$  Considering the Intermediates  $\text{NH}_3 \cdots \text{HF}$  and  $\text{H}_3\text{NH}^+ \cdots \text{F}^-$*

In this section of the study we examined the possible course of the reaction through the following intermediates: the neutral complex  $\text{NH}_3 \cdots \text{HF}$  and the ion pair  $\text{H}_3\text{NH}^+$

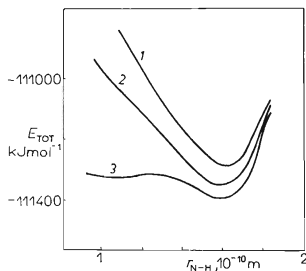


FIG. 1

Dependences of Total Energy  $E_{\text{TOT}}$  of  $\text{NH}_3\text{-HF}$  System on Interatomic Distance  $r_{\text{N-H}}$  for Various Solvation Coefficients  $k_{\epsilon_r}$  Calculated from the Solvation Model by Jano<sup>8</sup>

1  $k_{\epsilon_r} = 0$ , 2  $k_{\epsilon_r} = 0.2$ , 3  $k_{\epsilon_r} = 0.494$ .

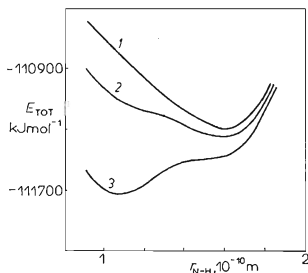


FIG. 2

Dependences of Total Energy  $E_{\text{TOT}}$  of  $\text{NH}_3\text{-HF}$  System on Interatomic Distance  $r_{\text{N-H}}$  for Various Solvation Coefficients  $k_{\epsilon_r}$  Calculated from the Solvaton Model

1  $k_{\epsilon_r} = 0$ , 2  $k_{\epsilon_r} = 0.2$ , 3  $k_{\epsilon_r} = 0.494$ .

$\cdots F^-$ . The solvent effect on stability of the both intermediates was followed by the dependence of the total energy of  $NH_3-HF$  system on the interatomic distance  $r_{N-H}$  at a constant distance  $r_{N-F} = 2.65 \cdot 10^{-10}$  m (the optimized value from the *ab initio* calculation<sup>3</sup>) at various relative solvent permittivities characterized by the so called solvation coefficient  $k_{\epsilon_r} = (1/2) \cdot (1 - 1/\epsilon_r)$ . The results are given in Figs 1 and 2 showing that in gas phase the interaction between  $NH_3$  and  $HF$  is of a H-bond nature, the system being most stable in the form of the neutral complex  $H_3N \cdots HF$ . Fig. 1 shows the hydrogen migration course taking into account only the electrostatic-coulombic contribution to the overall solvation energy of the system. Increasing solvent polarity causes two minima to appear corresponding to the two said intermediates, the neutral hydrogen complex being preferred in the aqueous phase ( $\epsilon_r = 80$ ,  $k_{\epsilon_r} = 0.494$ ). If also the polarization contribution is involved by means of the solvaton model, a more correct description of the situation is obtained, because it is reasonable to expect that formation of the ion pair represents a necessary stage in polar aqueous medium before dissociation to free ions (Fig. 2).

Solvent effect on the reaction course  $NH_3 + HF \rightarrow NH_4^+ + F^-$  was also studied by Noell and Morokuma<sup>4</sup> within the framework of the supermolecular model at the *ab initio* level. They found that the curve of the dependence of total energy on the distance between the migrating hydrogen atom and fluorine atom shows only one minimum belonging to the neutral complex. The authors<sup>4</sup> presume that involvement of hydration of the central region of  $NH_3-HF$  system or introduction of contributions of further spheres would result in formation of a minimum at the curve of dependence of the total energy vs interatomic distance which would belong to the ionic complex  $H_3NH^+ \cdots F^-$  (as it is indicated in the approach used by us).

The results given in this communication show that the solvaton model in spite of its approximateness gives a true qualitative picture of the solvent effect on the studied reaction.

*The authors are indebted to Dr O. Kysel', Institute of Polymers, Slovak Academy of Sciences, Bratislava, for valuable suggestions.*

#### REFERENCES

1. *The Jerusalem Symposium on Quantum Chemistry and Biochemistry*, No 8 (B. Pullman, Ed.). Reidel Publishing Co., Boston 1976.
2. Clementi E.: *Lecture Notes in Chemistry*, Vol. 2. Springer, Berlin 1976.
3. Kollmann P., Kuntz I.: *J. Amer. Chem. Soc.* 98, 6820 (1976).
4. Noell J., Morokuma K.: *Chem. Phys. Lett.* 36, 465 (1975).
5. Germer H.: *Theor. Chim. Acta* 35, 273 (1974).
6. Miertuš S., Kysel' O.: *Chem. Phys.* 21, 27 (1977).
7. Miertuš S., Kysel' O.: *Chem. Phys.* 21, 33 (1977).
8. Jano I.: *C. R. Acad. Sci., Ser. D.* 261, 103 (1965).
9. Pople J. A., Beveridge D. L.: *Approximate Molecular Orbital Theory*. McGraw-Hill, New York 1970.

10. Rossini F.: *Selected Values of Thermodynamic Properties*, NBS-500, 1973.
11. Philips C., Williams R.: *Inorganic Chemistry I*. Oxford 1965.
12. Morris D.: *Structure and Bonding*, Vol. 4. Springer, Berlin 1968.
13. Miertuš S., Kysel' O.: Chem. Phys. Lett. 65, 395 (1979).

Translated by J. Panchartek.