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The Electrophile Desolvation Process in Nucleophile-Electrophile Combination Reactions*

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The protonation and methylation of ethylene in different solvents are studied, by means of the MINDO/3 method, in order to check the hypothesis of partial desolvation of the electrophile at the transition state. It has been found that the degree of desolvation depends on both the electrophile and the solvent. The consequences of these results are discussed.

INTRODUCTION

Some of Ritchie's papers¹⁻³ on nucleophile-electrophile combination reactions have shown that the nucleophilic activity of a large number of nucleophiles, in their reaction with electrophiles, is correlated by

$$\log k = \log k_0 + N_+$$

where k is the rate constant for a reaction of an electrophile with a given nucleophilic system, k_0 is dependent solely on the identity of the electrophile and N_+ is a parameter characteristic of the nucleophilic system. The most surprising result of this relation is its incompatibility with the reactivity-selectivity principle, because, since N_+ is independent of the electrophile, the relative reactivity of different electrophiles with a given nucleophilic system is constant and independent of said nucleophilic system, which implies that the selectivity of these kinds of reactions do not depend on their reactivity. To explain this fact, Ritchie concluded that there are not specific interactions between electrophile and nucleophile at the transition state, and that electrophile desolvation has not begun. On the contrary, Pross⁴ showed that experimental data could be interpreted much better by supposing that the electrophile had undergone partial desolvation at the transition state; the less extensive this desolvation the stronger the electrophile. Introducing the assumption that the degree of electrophile desolvation at the transition state is dependent

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only on the electrophile and not on the solvent, he comes to the conclusion that said degree of desolvation for a particular electrophile is inversely proportional to the difference in solvation energy of that electrophile in two solvents.

In order to clarify this controversy, theoretical calculations on the attack of the proton and CH_3^+ , both solvated with one water molecule, on ethylene and benzene, have been carried out.⁵⁻⁶ It was shown that a more extensive desolvation exists at the transition state in methylation than in protonation. These results clearly favor Pross's model; the desolvation being stronger the weaker the electrophile. The desolvation phenomenon manifests a very essential fact: that, since the solvent is also a nucleophile because of its electron-donor character, the attack of a solvated electrophile on a nucleophile may be considered as the transfer of the electrophilic agent from one nucleophile to the other. So the solvent does not appear as merely providing a physical environment for the reaction but also as a true reactant.

To study the influence of the solvent on Pross's model and, in particular, to check his hypothesis that the degree of electrophile desolvation at the transition state does not depend on the solvent, the protonation and methylation of ethylene in different solvents will be studied in this paper. From the results obtained, we shall be able to obtain a deeper insight into the fact that solvation parameters are a part of the reaction coordinate at the transition state.

METHOD OF CALCULATION

Given the impossibility of calculating the potential hypersurface for the majority of reactions of chemical interest, a good approximation consists in taking one or two geometric parameters as independent variables in order to reduce the dimension of the potential hypersurface. For each value of the independent variables, all the remaining geometric parameters of the system are optimized. Because of the number of parameters to be optimized the semi-empirical MINDO/3 method⁷ has been chosen in order to maintain the computation time within reasonable limits. Dewar's MINDO/3 program⁸, in which the geometric optimization is carried out by means of the Davidon-Fletcher-Powell algorithm,⁹⁻¹⁰ has been used.

To study the effect of solvation, the supermolecule model has been employed, the electrophile being solvated with just one solvent molecule placed on the side opposite to the direction of attack.

RESULTS AND DISCUSSION

For the C_2H_5^+ and C_3H_7^+ cations, the MINDO/3 method, optimizing all the geometric parameters, shows that the π complexes are more stable than the σ complexes. These results are in good agreement with the experimental data¹¹ and with the ab initio calculations in which the correlation energy has been taken into account.¹²⁻¹⁶ For this reason, only the formation of the π complexes will be studied, imposing the restriction that the attacking H or C atom of the electrophile remain over the middle point of the C—C bond in ethylene.

Given that the objective of this paper is to clarify the participation of the solvation parameters in the reaction coordinate, both the distance from the nucleophile to the electrophile, d , and the distance from the electrophile to the solvent, D , (see Figure 1) must necessarily be chosen as independent variables. In Figure 2 we present the potential surfaces obtained using water as solvent, for the formation of π complexes in the protonation (Figure 2a) and methylation (Figure 2b) of ethylene. On both potential surfaces a more advanced transition state can be observed in the case of methylation than in

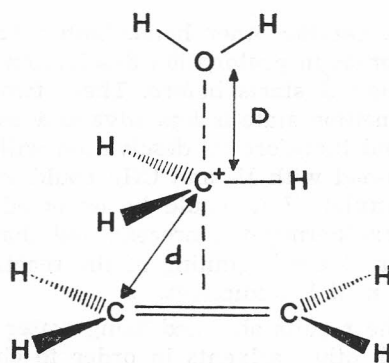


Figure 1. Arrangement of nucleophile-electrophile-solvent system.

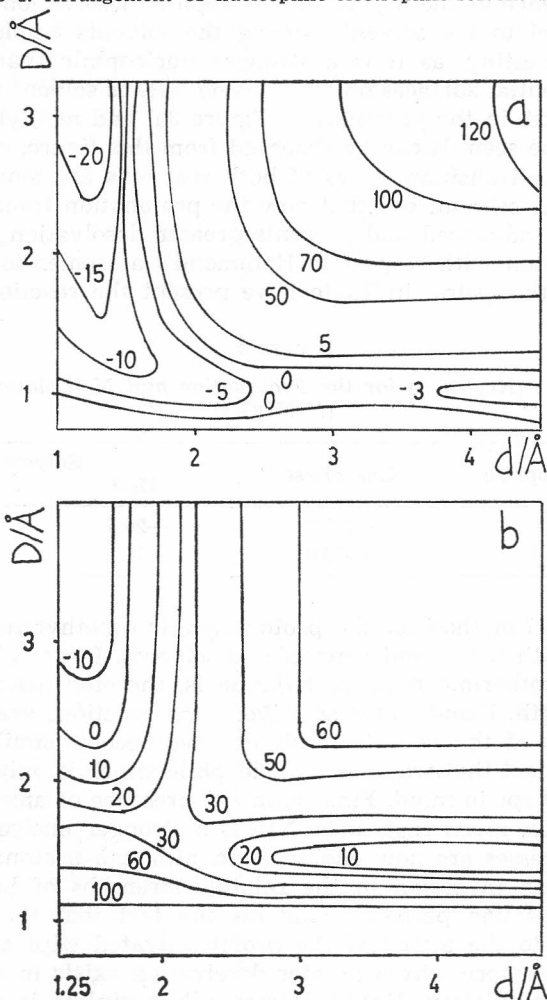


Figure 2. Potential surfaces for the formation of the π complexes in the a) protonation and b) methylation of ethylene using water as solvent. d is the a) proton-carbon or b) $C-CH_3'$ distance and D is the a) proton-oxygen or b) $CH_3^+-OH_2$ distance. The scaling of isoenergetic lines is given in Kcal/mol.

the case of protonation. On the other hand, both reactions are accompanied by desolvation, but, whereas in protonation desolvation begins after the transition state, in methylation it starts before. These two aspects are obviously related, since, if the transition state is less advanced, said transition state will be more reactant-like and therefore its desolvation will also be less advanced. In fact, the results obtained with H^+ and CH_3^+ could easily be generalized, in light of Hammond's postulate:¹⁷ it would be expected that the stronger the electrophile, the more exothermic the process, and that, therefore, the transition state would appear at the beginning of the reaction coordinate, in good agreement with Pross's model predictions.

Having presented the results obtained using water as solvent, let us analyze those obtained with other solvents in order to check Pross's hypothesis on the independence of the degree of electrophile desolvation at the transition state with respect to the solvent. Among the solvents employed ammonia is particularly interesting, as it is a stronger nucleophile than ethylene is. In Figure 3 the potential surfaces obtained using NH_3 as solvent for the formation of the π complexes in the protonation (Figure 3a) and methylation (Figure 3b) of ethylene can be seen. It can be observed from this figure, comparing it with Figure 2, that the transition states of both reactions are more advanced than when water is the solvent, but that now the protonation transition state is the one that is more advanced and presents greater desolvation, which is an apparent contradiction with respect to Hammond's aforementioned postulate. In order to clarify this point, in Table I we present the reaction heats obtained

TABLE
Reaction Heats (Kcal/mol) for the Protonation and Methylation of Ethylene (MINDO/3)

Electrophile	Gas phase	Solvent	
		H_2O	NH_3
H^+	-157.9	-20.5	22.4
CH_3^+	-82.9	-16.1	15.2

with the MINDO/3 method for the protonation and methylation of ethylene in gas phase and with water and ammonia as solvents. In gas phase, protonation is much more exothermic than methylation is, therefore each electrophile has a different strength. Using water as solvent, the reactions are still exothermic but the strengths of the two electrophiles have become similar, which is not so strange if the fact that water is a nucleophile which is only slightly weaker than ethylene is kept in mind. Finally, in the presence of ammonia a dramatic change takes place, given that, since NH_3 is a stronger nucleophile than ethylene is, both processes are now endothermic, although protonation is more so; in other words, an inversion in the relative strengths of both electrophiles appears. This inversion perfectly explains the fact that the transition state that corresponds to the attack of the proton solvated with ammonia is more advanced, and therefore why a greater desolvation exists in this process than in the case of methylation. Hence, Hammond's postulate is not contradicted. In conclusion, given that the attack of a solvated electrophile on a nucleophile is equivalent to the transfer of the electrophilic agent from one nucleophile

to the other, we can affirm that the reaction will be either endothermic or exothermic if the solvent has a greater or lesser nucleophile nature, respectively, than the nucleophile that is attacked. In both cases, the stronger the electrophile, the more endothermic or exothermic the reaction will be.

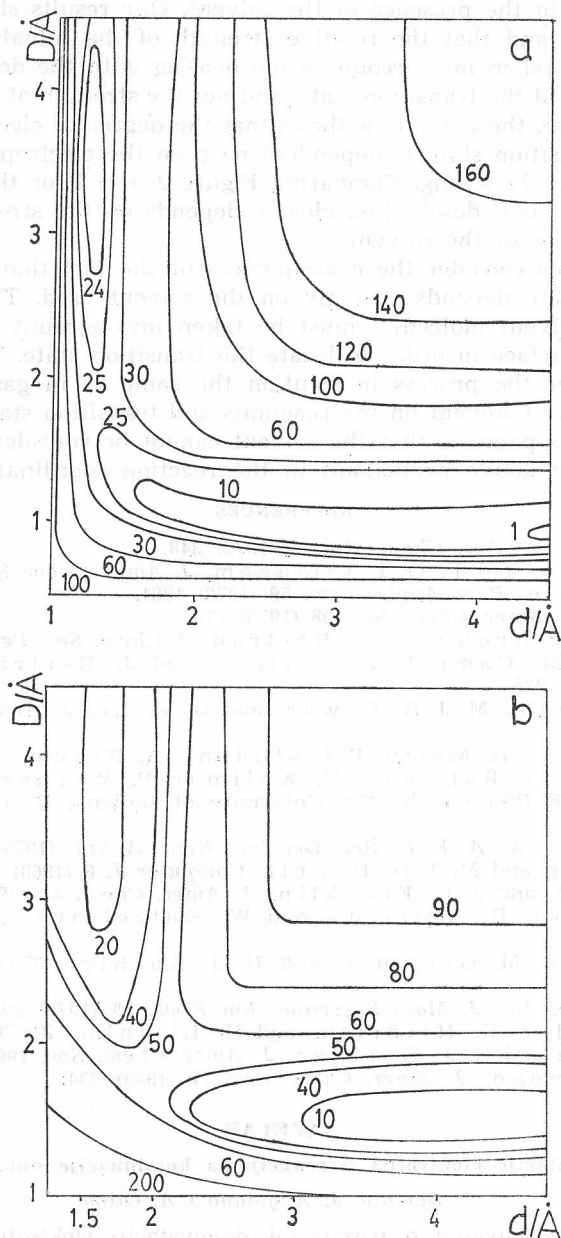


Figure 3. Potential surfaces for the formation of the π complexes in the a) protonation and b) methylation of ethylene using ammonia as solvent. d is the a) proton-carbon or b) $C-CH_3^+$ distance and D is the a) proton-nitrogen or b) $CH_3^+-NH_3$ distance. The scaling of isoenergetic lines is given in Kcal/mol.

Now let us discuss Pross's idea that electrophile desolvation at the transition state is less extensive the stronger the electrophile. Pross takes as the electrophilic reactivity order the one corresponding to gas phase, as studies conducted with different solvents lead him to suppose that said order will remain constant in the presence of the solvent. Our results show that this is not always true, and that the relative strength of the solvated electrophiles is what must be taken into account when dealing with the degree of electrophile desolvation at the transition state, and not the strength of isolated electrophiles. In any case, the Pross hypothesis that the degree of electrophile desolvation at the transition state is dependent only on the electrophile and not on the solvent is clearly wrong. Comparing Figure 2 and 3 for the same electrophile-nucleophile pair, desolvation clearly depends on the stronger or weaker nucleophilic nature of the solvent.

Finally, let us consider the consequences of the fact that the position of the transition state depends strongly on the solvent used. This implies that reactants and solvent molecules must be taken into account together on the potential hypersurface in order to locate the transition state. Then, it is erroneous to consider the process in solution the same as in gas phase just by adding the effect of solvent on the reactants and transition state. So, the main conclusion of this paper is that the solvent cannot be considered as a passive spectator, but an active participant in the reaction coordinate.

REFERENCES

1. C. D. Ritchie, *Acc. Chem. Res.* **5** (1972) 348.
2. C. D. Ritchie and P. O. I. Virtanem, *J. Amer. Chem. Soc.* **94** (1972) 4966.
3. C. D. Ritchie, *Pure Appl. Chem.* **50** (1978) 1281.
4. A. Pross, *J. Amer. Chem. Soc.* **98** (1976) 776.
5. T. Sordo, M. Arumi, and J. Bertrán, *J. Chem. Soc. Perkin II* (1981) 708.
6. T. Sordo, M. Campillo, A. Oliva, and J. Bertrán, *Chem. Phys. Lett.* **85** (1982) 225.
7. R. C. Bingham, M. J. S. Dewar, and D. M. Lo, *J. Amer. Chem. Soc.* **97** (1975) 1285.
8. M. J. S. Dewar, H. Metiu, P. J. Student, A. Brown, R. C. Bingham, D. M. Lo, C. A. Ramsden, H. Kollmar, P. Werner, and P. K. Bischof, *QCPE Program No 279*, University of Indiana, Bloomington, Indiana, USA.
9. W. C. Davidon, *A. E. C. Res. Develop. Rept. A.N.I.* (1959) 5990.
10. R. Fletcher and M. J. D. Powell, *Computer J.* **6** (1963) 163.
11. S. L. Chong and J. L. Franklin, *J. Amer. Chem. Soc.* **94** (1972) 6347.
12. B. Zurawski, R. Ahlrichs, and W. Kutzelnigg, *Chem. Phys. Lett.* **21** (1973) 309.
13. D. Heidrich, M. Grimmer, and H. J. Koehler, *Tetrahedron* **32** (1976) 1193.
14. J. A. Pople, *Int. J. Mass Spectrom. Ion Phys.* **19** (1976) 89.
15. H. J. Koehler, D. Heidrich, and H. Lischka, *Z. Chem.* **17** (1977) 67.
16. H. Lischka and H. J. Koehler, *J. Amer. Chem. Soc.* **100** (1978) 5297.
17. G. S. Hammond, *J. Amer. Chem. Soc.* **77** (1955) 334.

SAŽETAK

Proces desolvatacije elektrofila u reakcijama kombinacije nukleofil-elektrofil

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Radi provjere hipoteze o parcijalnoj desolvataciji elektrofila u prijelaznom stanju, s pomoću postupka MINDO/3 ispitivano je protoniranje i metiliranje etilena u različitim otapalima. Nađeno je da stupanj desolvatacije ovisi i o elektrofilu i o otapalu. Razmatrane su posljedice tih rezultata.