Relaxation of Solvent in Nucleophile–Electrophile Combination Reactions

J. Anguiano
Dpto. de Química-Física, Universidad de Sevilla, Sevilla, Spain
J. Bertrán
Dpto. de Química-Física, Universidad Autónoma de Barcelona, Bellaterra, Barcelona, Spain

A MINDO/3 study has been made of electrophile solvation during nucleophile–electrophile combination in solution. The results show that movements both of the molecules of the solvent linked to the electrophile and of those of the second layer form parts of the reaction co-ordinate.

The part played by the solvent[1] in nucleophile–electrophile combination reactions is the key to interpreting correctly experimental results which, apparently, contradict the reactivity–selectivity principle.[2–4] In previous theoretical studies,[5–8] taking ethylene as the nucleophile and employing different electrophiles, solvated with a single solvent molecule, it has been found that the degree of desolvation in the transition state depends simultaneously on the electrophile and on the solvent. The solvation parameter forms part of the reaction co-ordinate so that an active role must be assigned to the solvent in the process. In reality, since the solvent acts as a nucleophile, it is also behaving like a chemical reagent. The process consists in the transference of the electrophile from one nucleophile to another.

Marcus[9,10] and Levich[11] have also assigned an active role to the solvent in outer-sphere electron-transfer reactions. The relaxation of the solvent defined the reaction co-ordinate at the actual stage of electron-transfer. However, the active role attributed to the solvent does not mean that it is acting as a chemical reagent, in contrast with the findings of our previous theoretical studies.[5–8] This theory was later extended[12,13] to include proton-transfer processes. Recently we have shown in a theoretical study that solvation parameters also form part of the reaction co-ordinate in the transfer of methyl in a Walden inversion reaction.[14]

Since a single solvent molecule placed in reactions involving nucleophile–electrophile combinations is seen to act as a nucleophile, the process apparently consists of the transfer of the electrophile from one nucleophile to another. The aim of the present study is to discover whether Marcus and Levich's theory can be extended to include these processes. To this end, we have investigated the effects of solvating the single solvent molecule referred to earlier with more solvent molecules. We have used H^+ as electrophile, ethylene as nucleophile, and water and ammonia as solvents.

Method

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 geometrical parameters as independent variables in order to reduce the dimensions of the potential hypersurface. For each set of values of the independent variables all the remaining geometrical parameters of the system are optimized. Because of the number of parameters, to optimize the results the semi-empirical MINDO/3 method[15] has been chosen. The GEOMO program of Rinaldi[16] was used.

To study the effect of solvation, the supermolecule model was employed. The electrophile H^+ is solvated with one molecule of water or ammonia, placed in the direct line of attack, and, at the same time, this solvent molecule is solvated with other molecules of the same solvent, forming hydrogen bonds.

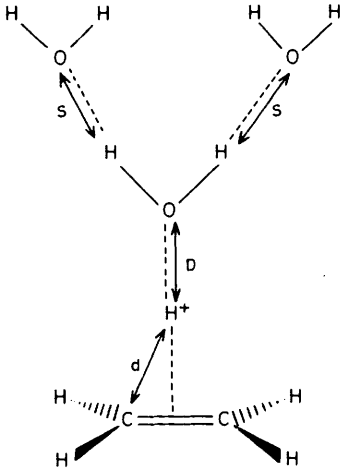

Figure 1. Basic geometric parameters in the C_2H_4–H^+–$(H_2O)_3$ system

Results and Discussion

To complement the previous studies,[5–8] the formation of the π-complex will be analysed. In the case of both the MINDO/3 method[5] and the *ab initio* methods, upon introducing the energy correlation,[17–21] the π-complex of the type $C_2H_5^+$ is more stable than the σ-complex. We will first discuss the attack of H^+ solvated with one molecule of water which, at the same time, is solvated with another two, forming hydrogen bonds.

Figure 1 shows an outline of the basic parameters that define the system: *d* is the distance of the H^+ from the carbon atoms of ethylene; *D* is the distance of the H^+ from the oxygen molecule of water; and *S* is the distance between the hydrogen atoms of this molecule of water and the oxygen atoms of the other two molecules of water. Given the symmetry imposed upon the system, the two solvation parameters, *S*, of the two molecules of water, together with their geometries, are identical.

Figure 2 contains the reduced potential-energy surfaces, obtained by using *d* and *D* as independent variables. Figure 2(a) refers to the C_2H_4–H^+–H_2O system and Figure 2(b) the C_2H_4–H^+–$(H_2O)_3$ system. This most obvious difference is the appearance of an intermediate in Figure 2(b). A similar intermediate had been observed previously in a study of H^+ attack on ethylene solvated with a molecule of nitromethane,[22] and was attributed to the fact that ethylene and nitromethane have similar proton bonding. Although the proton bonding of a molecule of water is much less than that of ethylene, when the number of water molecules is increased the proton bonding increases and becomes like that of ethylene; thus the appearance of an intermediate can be similarly explained.

Table 1 shows the energies of the separate reagents and the values of the parameters *d*, *D*, and *S* for the fixed points of both

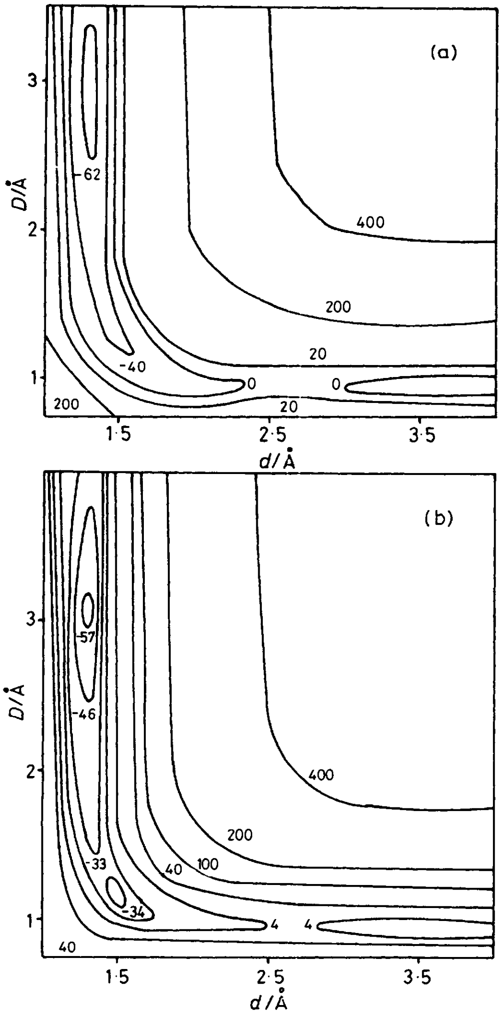

Figure 2. Reduced potential-energy surfaces for the formation of π-complexes (a) for the C_2H_4–H^+–H_2O system and (b) for the C_2H_4–H^+–$(H_2O)_3$ system; the isoenergetic scaling is given in kJ mol^{-1}

surfaces. Also the Table shows the corresponding values for the C_2H_4–H^+–$(H_2O)_3$ process without allowing for the relaxation of the parameter *S*.

Comparison of the first two processes shows a slight increase in the potential energy barrier from 3.30 to 4.81 kJ mol^{-1}. Further, the parameter *d* moves from 2.70 to 2.60 Å, representing a delay in the transition state throughout the reaction co-ordinate. Both these results are justifiable since the new water molecules hold up the transfer of the proton. This also results in decreased exothermicity. These results agree with Hammond's postulate since in the second process the transition state is less like that of the reagents. In the second process the step from the intermediate to the products shows a barrier of 1.68 kJ mol^{-1}. In view of this, it is scarcely possible to consider the reaction as a two-stage process.

Changes in the parameters *D* and *S* run closely parallel to one another. In view of this it may be supposed that the relaxation parameter *S* also forms part of the reaction co-ordinate in a similar way to parameter *D*. A reduced potential-energy surface, with *d* and *S* as independent variables, is seen to be similar to Figure 2(b), showing clearly that the parameter *S* forms part of the reaction co-ordinate.

The importance of relaxation in the parameter *S* in the process of proton transfer is shown by Figure 3, which presents the reduced surface, with *d* and *D* as independent variables, but with the parameter *S* at a fixed distance from the reagents. Figure 3 shows similarities to Figure 2(b). However, from Table 1, notable quantitative differences in the final stage of the process are observed. Both in the intermediate and in the second transition stage, as well as in the products, clear instability is produced, the process being much less exothermic. The potential barrier during the step from the intermediate to the products is now 5.44 kJ mol^{-1}, the intermediate thus revealing a greater kinetic stability. Since the relaxation of the solvation parameter *S* is held up, proton transfer from the water molecule to the ethylene is made even more difficult.

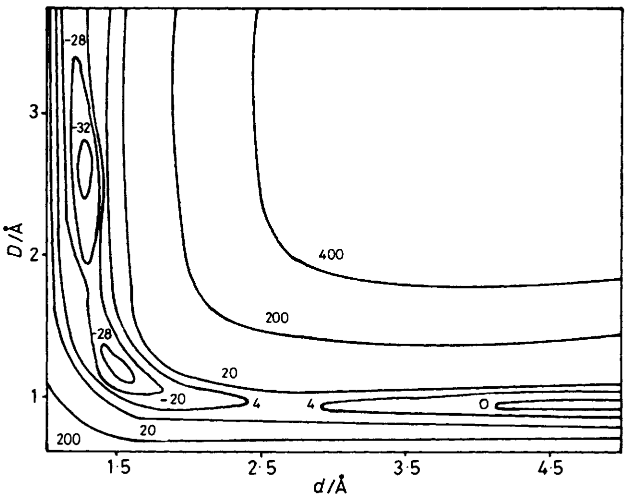

Figure 3. Reduced potential-energy surface for the formation of a π-complex for the C_2H_4–H^+–$(H_2O)_3$ system, keeping the parameter *S* a fixed distance from the reagents; the isoenergetic scaling is given in kJ mol^{-1}

The participation of the parameter *S* in the reaction co-ordinate is underlined in Table 2. With the intermediate as the point of departure, *S* was chosen as the independent variable while the rest of the geometric parameters in the system were left to find their own optimum levels, *d* and *D* thus doing so as well. As the parameter *S* increases, so the energy decreases slightly until for the value $S = 4.04$ Å a sharp drop in energy is produced. From this point on the energy continues to decrease until the final products are reached. If the changes in the parameters *d* and *D* are studied closely, it may be seen that this sharp drop in energy is linked with the transfer of the proton from the water molecule to ethylene. As a result, with the single variation of the solvation parameter *S*, the transfer of the proton is produced spontaneously.

This spontaneous transfer of the proton by modification of the solvation parameter *S* is seen even more clearly in the C_2H_4–H^+–$(NH_3)_4$ system. Here the proton is solvated by an ammonia molecule which, at the same time, is solvated with three other molecules, forming hydrogen bonds. The transfer of the proton from an ammonia molecule to ethylene[7] was clearly an endothermic process, such that, in keeping with Hammond's postulate, the transition state was similar to the final products. Upon solvating the ammonia molecule with three others, the transfer of the proton from ethylene to ammonia is enhanced. However, the potential barrier, which still exists, prevents the process being carried through spontaneously. From the minimum-energy point on, where H^+ is found above ethylene, and with the parameter *S* as independent variable, the values indicated in Table 3 have been obtained. As *S* decreases so the energy increases until the system suddenly becomes stable at the value $S = 1.40$ Å. This sharp energy change is linked with the transfer of the proton from ethylene to ammonia. Once again

Table 1. Energies of the reagents; values of *d*, *D*, and *S* for the fixed points of the surfaces shown in Figures 2a, 2b, and 3

		E/kJ mol^{-1}	d/Å	D/Å	S/Å
C_2H_4–H^+–H_2O	Reagents	1.79	4.05	0.96	
	TS	3.30	2.70	0.97	
	Products	−69.92	1.29	2.91	
C_2H_4–H^+–$(H_2O)_3$	Reagents	−0.28	5.04	0.96	2.81
	TS1	4.81	2.60	0.97	2.82
	Intermediate	−34.81	1.45	1.22	3.34
	TS2	−33.93	1.38	1.35	3.37
	Products	−57.86	1.29	3.05	4.69
	Reagents	−0.28	5.04	0.96	2.81
	TS1	4.89	2.58	0.97	2.81
	Intermediate	−30.87	1.47	1.19	2.81
	TS2	−25.43	1.34	1.45	2.81
	Products	−34.14	1.29	2.57	2.81

Table 2. Changes in energy and in *d* and *D* with *S* as independent variable in the C_2H_4–H^+–$(H_2O)_3$ system

S/Å	E/kJ mol^{-1}	d/Å	D/Å
3.34	−34.81	1.45	1.22
3.44	−35.02	1.45	1.22
3.54	−35.10	1.44	1.23
3.64	−35.31	1.43	1.24
3.74	−35.48	1.41	1.27
3.84	−35.68	1.40	1.30
3.94	−35.77	1.39	1.32
4.04	−54.68	1.29	2.82
4.14	−56.14	1.29	2.86
4.24	−56.60	1.29	2.86
4.34	−56.98	1.29	2.87
4.44	−57.27	1.29	2.87
4.54	−57.57	1.29	2.87
4.64	−57.80	1.29	2.88

Table 3. Changes in energy and *d* and *D* with *S* as independent variable in the C_2H_4–H^+–$(NH_3)_4$ system

S/Å	E/kJ mol^{-1}	d/Å	D/Å
5.00	101.08	1.29	4.00
4.50	101.58	1.29	4.00
4.00	103.01	1.29	4.00
3.50	107.06	1.29	4.00
3.00	117.31	1.29	4.00
2.50	141.92	1.29	3.99
2.00	194.38	1.29	3.99
1.90	209.61	1.29	3.99
1.80	227.19	1.29	3.98
1.70	247.86	1.29	3.98
1.60	272.83	1.29	3.97
1.50	304.67	1.29	3.96
1.40	9.62	5.40	1.03
1.30	28.53	5.40	1.03

the single variation in the solvation parameter S is enough to cause the spontaneous transfer of the proton. As a result it may be affirmed that H^+ adjusts its position according to the movement of the solvent.

Although the MINDO/3 method undervalues the solvation energies, it is useful enough to describe the phenomena of desolvation of the electrophile in the reactions involving nucleophile–electrophile combinations in solution. Previously it has been shown that while the electrophile is solvated with a molecule of solvent, this latter molecule has a chemical role in the process due to its nucleophile character. As a result the chemical reaction may be described as the transfer of an electrophile from one nucleophile to another. In the present study, where one molecule of solvent is solvated with others, it has been shown that the geometric parameters of the second solvation shell play a part on the reaction co-ordinate. The expansion of the solvation shell makes the transfer of the electrophile to ethylene easier, while the contraction of this shell makes the transfer of the electrophile from ethylene to the solvent easier. This process is similar to the way in which solvent relaxation plays a part in the processes of electron transfer according to the theories of Marcus and Levich. To sum up, it may be stated that, to a certain extent, H^+ adjusts its position according to the movement of the solvent molecules which make up the second solvation shell. As a result the active part played by the solvent in the chemical process is not only of a chemical nature; it is of a much more general kind.

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Received 16*th January* 1985; *Paper* 5/087