Theoretical Study of the Effect of Nitromethane on C_2H_4–H^+ and C_2H_4–CH_3^+ Combination Reactions

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The protonation and methylation of ethylene with solvation of the electrophile by one nitromethane molecule are studied, by means of the MINDO/3 method, in order to check the hypothesis of partial desolvation of the electrophile in the transition state. It has been found that the degree of desolvation depends on the electrophile, the solvent, and the nucleophile.

Ritchie's papers [1–3] 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 the nucleophilic system. This implies that the selectivity of these kinds of reactions does 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. In contrast, Pross [4] showed that the experimental data could be interpreted much better by supposing that the electrophile had undergone partial desolvation in the transition state; the less extensive this desolvation the stronger the electrophile. Introducing the assumption that the degree of desolvation of the electrophile in the transition state is dependent only on the electrophile and not on the solvent, he came to the conclusion that the 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 a proton and CH_3^+, both solvated either with one water molecule or with one ammonia molecule, on ethylene have been carried out.[5–7] In these studies Ritchie's hypothesis has been proved wrong. Pross's hypothesis is seen to be correct when water is taken as solvent, but it is not seen to be correct when ammonia is used as solvent. Since water is clearly a weaker nucleophile than ethylene, while, on the other hand, ammonia is a much stronger one, it would seem to be of interest to study the effect of a solvent with nucleophilic character similar to that of ethylene. In this way an overall picture may be obtained of the relation between solvation and the solvent used. Nitromethane shows a slightly higher proton- and methylene-affinity than ethylene and, as a result, is the appropriate solvent with which to complete our study.

Methods

Given the impossibility of calculating the total potential hypersurface for the majority of reactions of chemical interest, there are two basic approximations which help in overcoming this difficulty. The first consists of reducing the dimensions of the surface, and the second of locating directly the most interesting points on it. Both approximations are used in the present work.

To reduce the dimensions of the potential surface, one or two geometrical parameters are taken as independent variables. For each value of the independent variables all the remaining geometrical parameters of the system are optimized. Because of the number of parameters to optimize, the semiempirical MINDO/3 method [8] has been chosen in order to maintain the computation time within reasonable limits. Dewar's MINDO/3 program [9] and the GEOMO program of Rinaldi [10] have been used.

The direct location of the stationary points on the potential surface has been made by the method proposed by McIver and Komornicki [11] by means of the SIGMA program which minimizes the gradient norm. In a later step, using the FORCE program which diagonalizes the force constant matrix, the nature of those points is determined.

To study the effect of solvation, the supermolecule model [12] 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 π complexes are more stable than σ complexes. These results are in good agreement with the experimental data [13] and with *ab initio* calculations in which the correlation energy has been taken into account.[14–18] 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 remains over the mid-point of the C–C bond in ethylene.

In Figure 1 we show in comparative terms the reaction path that corresponds to the formation of the π complexes between the ethylene molecule and the electrophiles. The parameter d represents the distance either from the proton or from the carbon atom in CH_3^+ to the C atoms in ethylene, E being the energy in relation to the reactants. For a proton the process is very exothermic, no energy barrier being obtained. This is a logical result since a proton does not have an electron cloud and, therefore, Pauli's forces of repulsion do not appear. For CH_3^+ the process is less exothermic, a small potential barrier of 2.38 kJ mol^{-1} at 3.7 Å being obtained. Since CH_3^+ has an electron cloud, forces of repulsion are observed.

Let us now study the effect of solvation by a molecule of nitromethane on the mechanism of both reactions. Given that the objective of this paper is to clarify the participation of the solvation parameters in the reaction co-ordinate, both the

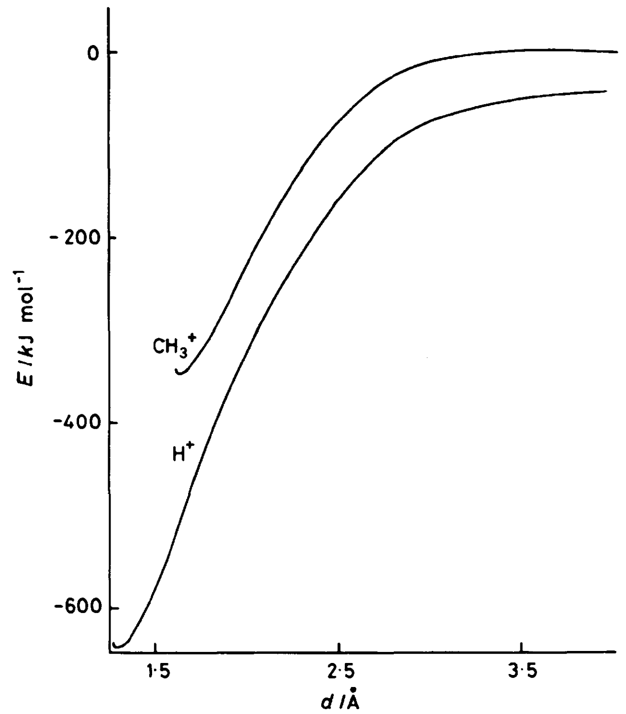

Figure 1. Formation of π complexes $C_2H_5^+$ and $C_3H_7^+$: d is the distance between the electrophile and C atoms of ethylene.

distance from the nucleophile to the electrophile, d, and the distance from the electrophile to the solvent, D, specifically the distance of the proton or the carbon atom in CH_3^+ and an oxygen atom in nitromethane, must necessarily be chosen as independent variables. In Figure 2 we present the potential surfaces obtained in the protonation of ethylene (Figure 2a) and methylation (Figure 2b).

In the case of protonation, a further intermediate with quite a symmetrical structure is seen to appear besides the initial and final intermediates. As a result of the presence of this intermediate, two transition states appear. On the other hand, in the case of CH_3^+ no symmetrical intermediate appears, and a single transition state is obtained, as when solvating H^+ CH_3^+ with a molecule of water or ammonia.[5–7]

On both potential surfaces the reaction co-ordinate has been shown by means of two variables only, d and D. This reduction may make the transition states obtained unreliable. By means of the SIGMA program, starting with the saddle-point geometries on the reduced surfaces, three stationary points on the complete hypersurface have been found, two for the proton and one for CH_3^+. Upon analysing their nature by means of the FORCE program, it has been discovered that the two stationary points for the proton show a single negative value on the matrix of force constants. Consequently, they are two real transition states. However, for CH_3^+ three negative values have been obtained. As a result it is not a real transition state. In this case, since more than one negative value appears on the matrix of force constants, Laidler–Murrell's[19] theorem assures us of the existence of a lower-energy saddle-point. In Figure 3 we show the components of the transition vector, in terms of each atom, for the two transition states in protonation. Also shown are the components of the vector itself which correspond to the most negative value for methylation.

In the case of the first transition state, it is observed that with regard to protonation (which is when H^+ is furthest away from ethylene), the reaction co-ordinate is defined by the approach of ethylene to solvent and of the electrophile towards ethylene. Both H^+ and oxygen have similar components which means the approach of the electrophile, at this point, is not accompanied by desolvation, as is observed on the surface in Figure 2a. The desolvation of the electrophile has hardly begun at the aforementioned point. On the other hand, in the second transition state of H^+ we observe that at this point the reaction co-ordinate consists of the departure of H^+ and C_2H_4 from the nitromethane molecule and, in turn, the departure of the nitromethane molecule from C_2H_4 and from H^+. This result confirms that at this point desolvation has already occurred, as may be observed on the surface. However, in this case, there was also a certain contribution of the approach of H^+ in ethylene as the reaction co-ordinate. In the case of CH_3^+, there is scarcely any variation in the distance between C_2H_4 and nitromethane

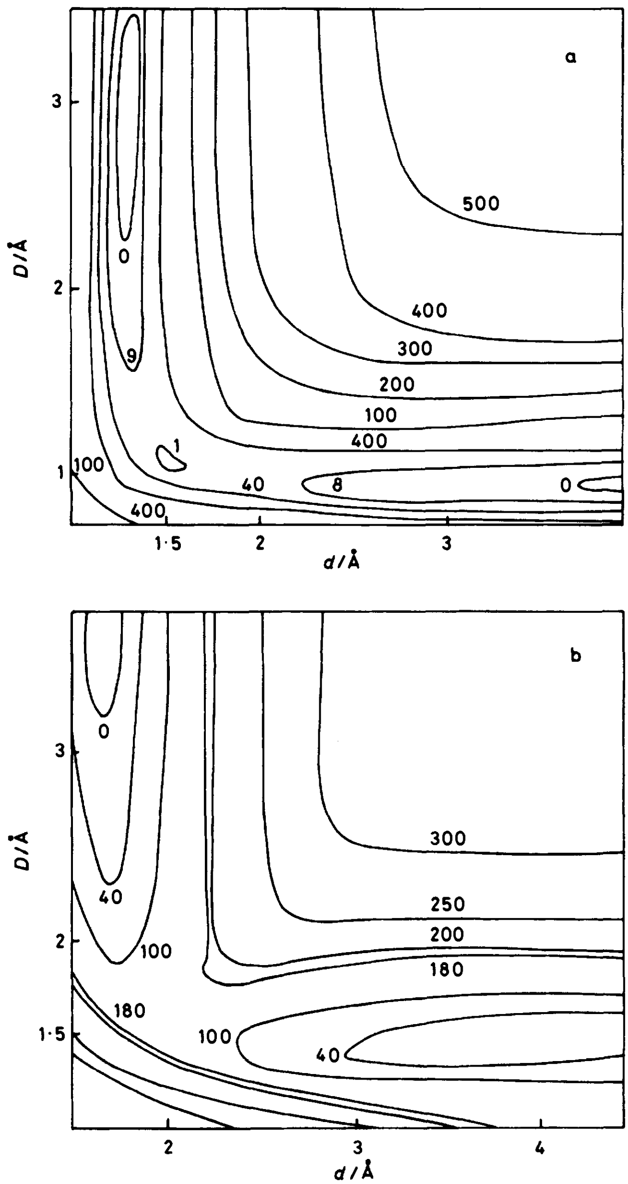

Figure 2. Potential surfaces for the formation of the π complexes in a, protonation and b, methylation of ethylene using nitromethane as solvent. d is the a, proton–carbon or b, C–CH_3^+ distance and D is the a, proton–oxygen or b, CH_3^+–oxygen distance. The scale of isoenergetic lines is given in kJ mol^{-1}

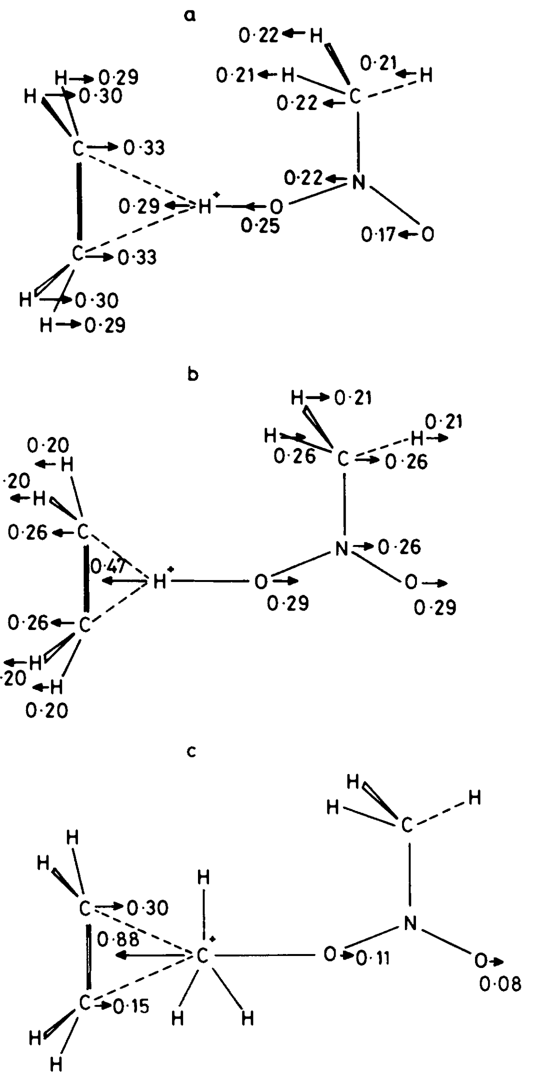

Figure 3. Components of the transition vector for the first a, and second b, transition states of ethylene protonation, and for the approximate transition state of ethylene methylation, c

and the reaction co-ordinate is similarly defined by the solvation parameter and the approach of CH_3^+ towards ethylene. In fact, in this transition state the transfer of CH_3^+ from nitromethane to ethylene is taking place. This is confirmed by what is shown in Figure 2b, *i.e.* partial desolvation in the transition state.

Comparing the results obtained during the methylation of ethylene, when methylene is solvated with water, ammonia, or nitromethane, it is proved that in the three cases there is a similar partial desolvation of the electrophile, this being slightly higher when the solvent is ammonia. In the three cases both the surfaces and the vector, which corresponds to the single most negative value on the matrix of force constants, are very similar. This shows that in this case, for the electrophile agent, CH_3^+, the desolvation of the electrophile hardly depends upon the solvent used.

Upon comparing the surfaces obtained for the protonation of ethylene, solvating H^+ with a molecule of water, ammonia,[5,7] or nitromethane, an overall divergence is observed in the three cases. It may be affirmed that the first transition state in nitromethane is similar to the only transition state obtained in solvation with water, while the second transition state is similar to the only transition state when the solvating molecule is ammonia. Identical results are observed when the transition vectors for the two transition states (Figures 3a and b) are compared with the corresponding vectors, at the most negative value, which appear in Figure 4.

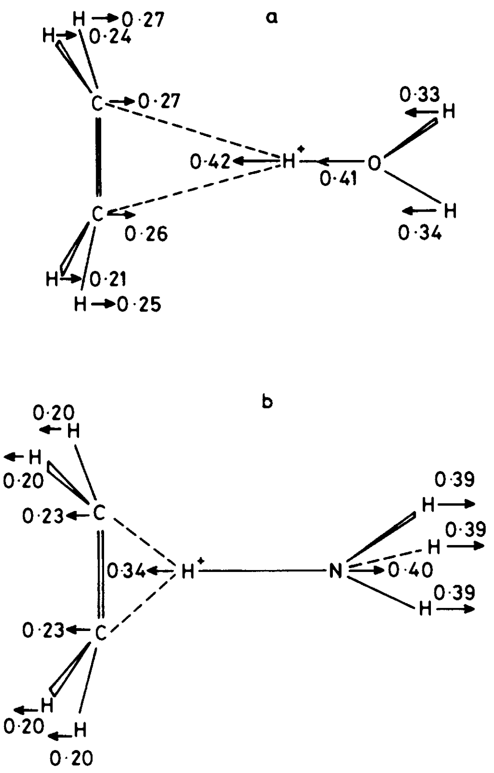

Figure 4. Components of the transition vector for the approximate transition states of ethylene protonation, solvating the electrophile with one water molecule, a, and with one ammonia molecule, b

It can be seen, therefore, that for a strong electrophile like H^+, the degree of desolvation in the transition state greatly depends upon the solvent. When the solvent is clearly less nucleophilic than the nucleophile, desolvation has hardly begun in the transition state. On the other hand, when the solvent is much more nucleophilic than the nucleophile, desolvation is seen to be at an advanced stage in the transition state. Also, in the case where the solvent may have a nucleophilic nature similar to that of the nucleophile, two transition states appear, one in which desolvation in the transition state does not appear and another in which it is found at a more advanced stage.

Thus it can be seen that when comparing the mechanism when a solvent is not present (Figure 1) with the process in which there are different solvents present, the first effect of solvation is to change the reaction mechanism radically. This change may be noticed especially when the electrophile is H^+. Above all, when the solvent has a nucleophilic character similar to that of the nucleophile, the change-mechanism is more outstanding since a close-approach intermediate appears. The appearance of this intermediate at short distances may be explained since, as a result of the peculiar electronic structure of H^+, Pauli's repulsion forces do not appear with the other two molecules.

In relation to the case studied, by solvating H^+ with nitromethane, we find an initial intermediate, of -1.25 kJ mol^{-1} with regard to the reactants, followed by a transition state of $+8.03$ kJ mol^{-1}, a second intermediate, of $+0.37$ kJ mol^{-1}, a second transition state, of $+9.07$ kJ mol^{-1}, and a final intermediate of

-3.17 kJ mol^{-1}. Also worthy of note is the parallelism of the surface obtained in the case of the transfer of H^+ between two molecules of water and the transfer of H^+ between a nitromethane molecule and one of ethylene. In the first case both nucleophiles are identical while, in the second, they are very similar. A close-approach intermediate, totally symmetrical, appears in the $H_5O_2^+$ species, in calculations using both semi-empirical and *ab initio* methods.[20–22]

In the light of the results obtained in the present study and in previous ones,[5–7] Ritchie's hypothesis, according to which the electrophile still hasn't desolvated in the transition state, has no foundation. However, Pross's hypothesis, according to which the degree of desolvation depends upon the electrophile, is false, above all in the case of strong electrophiles. In fact, the process of bonding between a nucleophile and an electrophile, in solution, should be considered as a transfer of the electrophile from one nucleophile to another. It is not surprising, then, that the distance of the electrophile from the solvent, which acts as a nucleophile, is fundamental in the reaction co-ordinate. The degree of desolvation in the transition state depends in turn, therefore, on the electrophilic character of the electrophile and the nucleophilic character both of the nucleophile and of the solvent.

Any simplification which does not keep these three factors in mind is unacceptable. We can see, then, that the solvent, due to its electron-donor character, acts as a real chemical reactant and plays an active role in the reaction co-ordinate.

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