

## THE REACTION OF CATIONS WITH ANIONS IN SOLUTION

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**Abstract** - Some general concepts involved in theories of solvent effects on ionic reactions in solution are discussed and some fallacies in extant theories are pointed out. The initial results of an exact treatment of a simplistic model for solvent effects on cation-anion combinations are presented. The model system consists of two charges and eight finite dipoles interacting through coulombic forces and  $[1/r]^{12}$  repulsions. Local minima in the potential energy surface of the system are found which correspond to "solvent-separated" ion pairs and "intimate" ion pairs, and reaction paths and saddle points connecting the species have been found.

### INTRODUCTION

The basic ideas of solvent effects on ionic reactions in solution are in likely need of radical change. Evidence has been mounting over a period of years which infer that the motion of the solvent molecules themselves are an important part of the motion along the reaction coordinate at the transition states for such reactions. If these inferences are correct, the naive view of transition state solvation being similar to solvation of stable species must be abandoned.

With the primary goal of developing some insight into the complex problem of cooperative solvent-solute motions, we have begun a study of model systems of cation-anion combinations in dipolar solvents. The initial results of a study of an extremely simplistic model of charges and finite dipoles emphasize some of the treacheries of most of the extant theories of solvent effects applied to real systems.

Before proceeding to the computational results, it will be worthwhile to examine some of the general features of solvent effects on ionic reactions, and to point out a fundamental fallacy that creeps into nearly all of the current theories.

### GENERAL CONCEPTS

Without much thought, one might conclude that the combination of an anion with a cation to form a neutral molecule is the simplest type of reaction imaginable. If this were true, it would be hard to appreciate the difficulties which we have met (1) in attempting to formulate a reasonable picture of the transition states for such reactions in solution. For example, any transition state picture which accommodates the observed insensitivity of electrophile-nucleophile combinations to coulombic effects is inconsistent with the observed sensitivity of the reactions to steric effects.

With a little more thought, some of the difficulties associated with ion combination reactions in solution become obvious. First, and most important, the entire existence of barriers to such reactions is almost certainly due exclusively to solvent effects. In the gas phase, the overwhelming magnitude of coulombic attractions is sufficient to virtually guarantee a complete absence of any points higher in energy than the separated ions as the two ions approach one another. Second, as shown most clearly in Kebarle's work (2), the binding energy of solvent molecules with ions is quite high. At least some of the solvent molecules must be stripped away if the two ions in solution are to contact one another.

The need for desolvation of ionic reactants has been recognized by most workers in this area for some time, but there is considerable confusion and disagreement concerning the timing of the desolvation. It may precede the transition state, follow the transition state, or, as we will develop below, it may be a fundamental part of the reaction coordinate at the transition state (3).

Certainly the most striking evidence indicating the necessity of treating solvent motion as an integral part of the reaction coordinate for ionic reactions is that recently presented by Caldin (4). A tremendous solvent effect on the magnitude of the kinetic deuterium isotope effect (ranging from ca. 10 to 50) in a simple proton transfer reaction was reasonably interpreted in terms of solvent molecules contributing to the reduced mass along the reaction coordinate. Other evidence includes our observations of negative activation entropies for both ion combination and ionic dissociation (5), and of solvent effects in the same direction for both combination and dissociation of ions (6).

The idea of solvent motion as a part of the motion along the reaction coordinate cannot be accommodated by most of the extant theories of solvent effects on reaction rates. This is because of a treacherous implicit assumption inherent in these theories. Although never, as far as I am aware, stated explicitly, virtually all of the present theories assume that a transition state is solvated in the same manner as would be a stable solute species having the same "structure". This is equivalent to stating that the energy of the transition state is at a minimum with respect to motion of solvent molecules; thus, solvent motion is not a part of the motion along the reaction coordinate.

The assumption is, at best, unwarranted, and in general, simply false. This can be seen quite easily by reference to the potential energy diagram shown in Fig. 1. For the sake of clarity, we consider a system in which there is a single solute coordinate and a single solvent coordinate. It will be shown later that the consideration of more coordinates does not change the conclusion to be reached, but such consideration does complicate the discussion.

In Fig. 1, the transition state is located at the point marked by the arrow. By definition, this is the highest energy point along the path indicated by the solid line connecting reactants and products. It is therefore obvious that the point marked X, vertically below the transition state, is of lower energy than the transition state. A stable species, having the solute coordinate the same as that of the transition state would, then, have the solvent coordinate equal to that of the point X.

In Fig. 1, as constructed, the motion along the reaction coordinate at the transition state is purely a solvent motion. If the maximum energy point were displaced in either direction along the reaction path, the reaction coordinate would contain contributions from both solute and solvent coordinates, and two points along the reaction path with the same value of the solute coordinate as the transition state would be of lower energy than the transition state.

I think it is also worthwhile here to point out that the formal application of thermodynamics to transition state theory for reactions in solution is particularly treacherous in inviting the above unwarranted assumption. For a reaction studied in two different solvents, or in the gas phase and a solvent, we may formally write:

$$\Delta G^* = \Delta G^0(\text{ts}) - \Delta G^0(\text{reactants}) \quad (1)$$

(or analogous equations for other thermodynamic functions) where the  $\Delta G^0$ 's are the transfer functions. The use of this equation is in obtaining the relative transfer function for the transition state. It is then easy to interpret this transfer function in analogy with some stable species. The possible fallacy in such interpretation should be clear from the above discussion.

This concept of solvent motion along the reaction coordinate forces us into a consideration of a complex system consisting of solute and some unknown number of intimately associated solvent molecules whose motions are correlated with those of the solute. In the hope of gaining some insight into such complex systems, we have begun a study of simple models of ionic reactions in solution which can be treated by exact methods.

#### COMPUTATIONAL RESULTS

The initial model chosen for study consists of two oppositely charged unit monopoles and eight finite dipoles interacting through coulombic forces and inverse twelfth power repulsions. The coefficients of the twelfth power repulsions are chosen to simulate particle sizes and to set these sizes so that no more than four dipoles ("solvents") can contact one monopole at the same time. The finite dipoles are chosen as charges of 30 units separated by 0.1 unit of length at the center of the particle. The units are arbitrary, but can be considered as atomic units, in which case the dipole moments of the dipoles are ca. 6 Debye, the radii of the dipoles are ca. 6 Angstroms, and the radii of the charges are ca. 2.5 Angstrom. The exact parameters chosen are:

$$\begin{aligned} \text{Monopole-monopole: } E &= E(\text{coulomb}) + [3.42/r]**12 \\ \text{Monopole-dipole: } E &= E(\text{coulomb}) + [8.00/r]**12 \\ \text{Dipole-dipole: } E &= E(\text{coulomb}) + [11.20/r]**12 \end{aligned}$$

The energy of this model system is a function of 40 non-trivial coordinates. Choosing a cartesian coordinate system, we place one monopole at the origin and the second on the X-axis. One dipole is placed in the XY-plane. Our forty coordinates then are: one coordinate for the distance between the two monopoles, an X and a Y coordinate for the location of the center of the first dipole, two dipole orientation angles for the first dipole, and three positional and two orientational coordinates for each of the remaining seven dipoles. Exact equations can be written for the energy, and for first and second derivatives of the energy as functions of coordinate values.

Local minima in the surface are located by searches along principal axes on the assumed locally quadratic surface. We find two local minima with quite large monopole-monopole separations. The configuration of the lowest energy one of these is shown in Figure 2. The monopole-monopole separation is 29.2942 units. The nearly perfect tetrahedra of dipoles around each monopole are slightly skewed from face-to-face contact. There is a C2 axis of

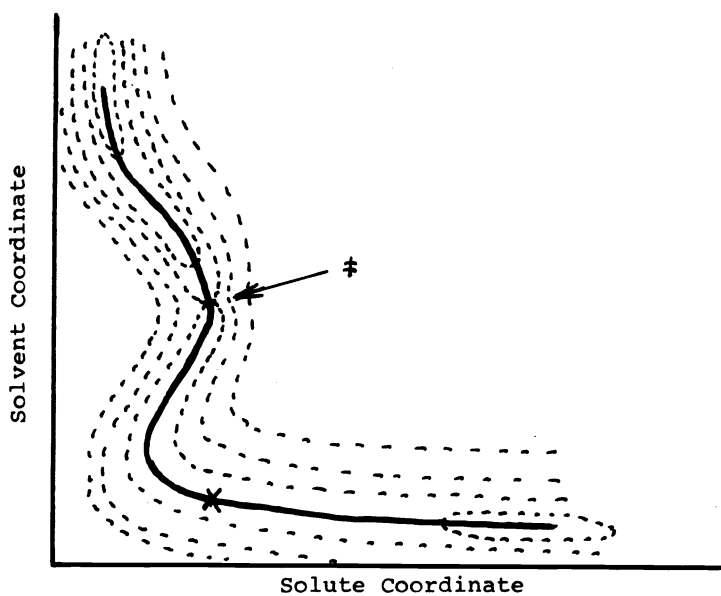


Fig. 1. A hypothetical potential energy surface for a reaction in solution.

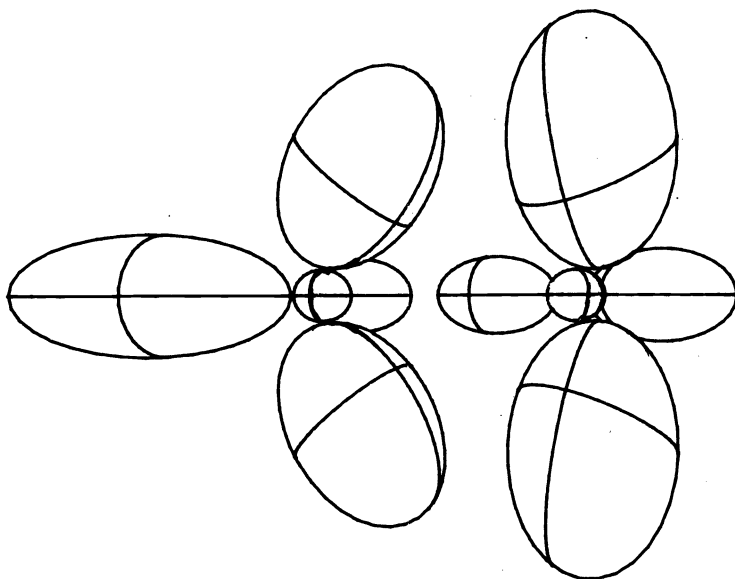


Fig. 2. A perspective drawing of the "reactant" configuration.

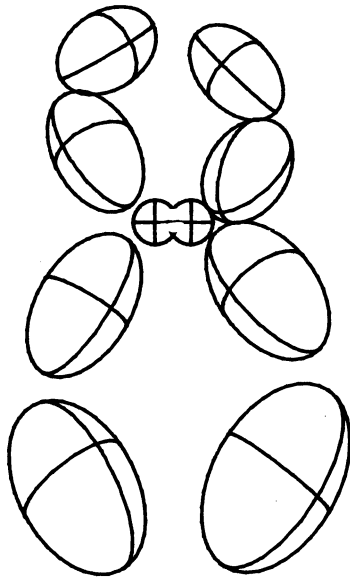


Fig. 3. A perspective drawing of the "product" configuration.

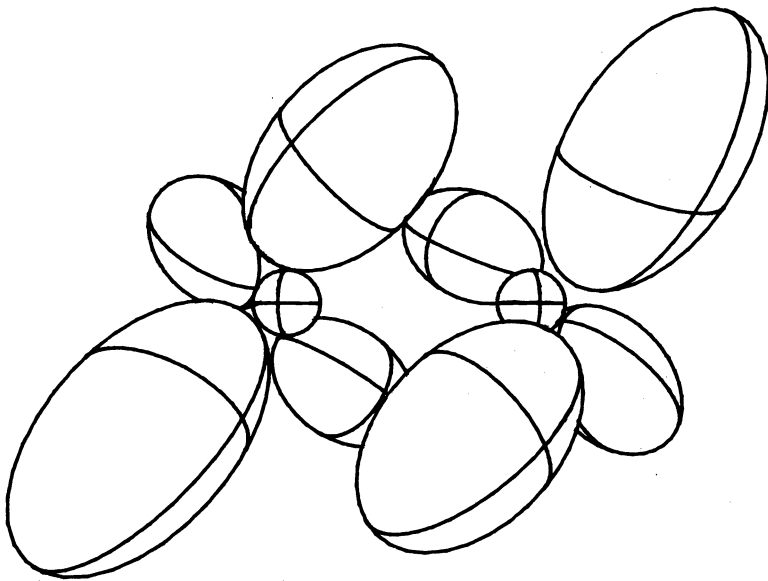


Fig. 4. A perspective drawing of the "classical" saddle point.

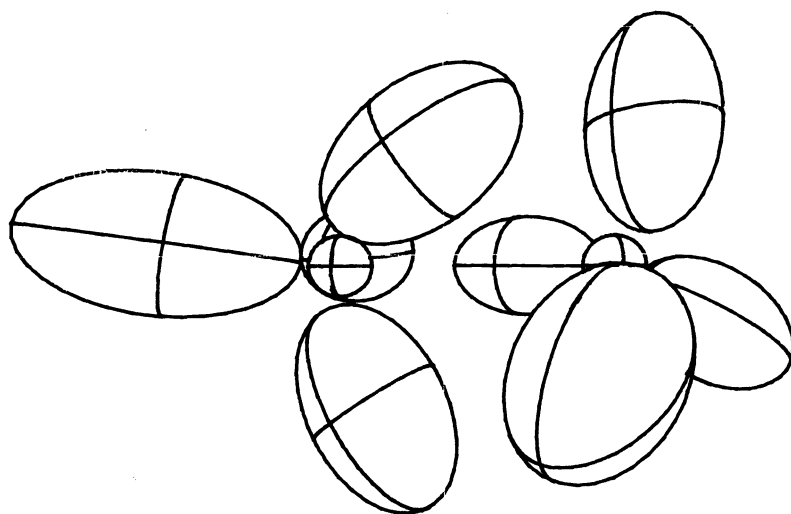


Fig. 5. A perspective drawing of the "non-classical" saddle point.

symmetry at right angles to the monopole-monopole axis. The energy of this configuration is  $-0.127858$  units.

We find a number of local minima with the two monopoles "touching". The lowest energy one of these is shown in Figure 3. The monopole-monopole separation is  $4.8374$  units, and the entire configuration is similar to that of the carbon skeleton of trans-decalin. The energy of the system is  $-0.217291$  units.

We now consider the configuration shown in Fig. 2 as a "reactant", and that shown in Fig. 3 as a "product", and find saddle points on reaction paths connecting the two points in the forty dimensional space.

The location of such saddle points is no trivial task, but we have succeeded in finding two different ones, both satisfying all the necessary criteria of being highest energy points along a path connecting reactant and product, having zero derivatives of energy with respect to all coordinates, and having one, and only one, negative eigenvalue of the second derivative matrix.

The saddle point having the configuration shown in Fig. 4 was located by minimizing energy of the system with respect to all coordinates except the monopole-monopole separation, which was held fixed at a series of values between those of reactants and products. The configuration has a monopole-monopole separation of  $22.3643$  units, and the slightly distorted tetrahedra of dipoles around each charge are oriented such that the tetrahedra meet at crossed edges. There is an  $S_2$  element of symmetry for this configuration. The energy of the system is  $-0.12702$  units. Although this method of location of saddle points is certainly not general, it does succeed for the present case.

We might refer to this configuration as a "classical" saddle point since it is located by minimizing energy with respect to solvent coordinates. Even here, however, it should be noted that the solvation is not equivalent to that of a stable species since the reaction coordinate (eigenvector with negative curvature) contains substantial contributions from solvent coordinates.

The saddle point having the configuration shown in Fig. 5 is of greater interest in connection with our earlier discussion. First, it is of lower energy than the one shown in Fig. 4. The reaction path is quite similar to that visualized in Fig. 1. The configuration has a monopole-monopole separation of  $27.0403$  units. There is no symmetry element in this configuration; the dipole at the upper-right of the figure has a unique orientation, and the motion along the reaction coordinate is composed almost purely of the coordinates of this one dipole. The energy of the system is  $-0.127250$  units.

This low energy transition state was located by what we believe to be a general method. First, energies for 100 configurations of the system lying along a straight line path between reactant and product are computed. The highest energy point is located, and a fine search is made of the line connecting this point to its two neighboring points for the exact maximum. The path at this point is then displaced by a small step in the direction of steepest descents (note that this is guaranteed to be orthogonal to the path). This entire process is reiterated until a highest energy point is found which cannot be displaced ortho-

gonally to the path to give a lower energy. Within the precision of the smallest step size allowed, this point is a saddle point. Its configuration can be refined to any desired precision by then subjecting it to a search for the minimum in the first derivative surface.

#### CONCLUSIONS

The most important finding in the computations presented above is that the situation envisaged in Fig. 1 actually applies to a physical system. Even when monopole-monopole forces are dominant in magnitude, as is this model, they are not sufficient to prevent the weaker monopole-dipole interactions from dictating the nature of the transition state.

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