A THEORETICAL STUDY OF SOLVENT EFFECTS ON THE RELATIVE THERMODYNAMIC STABILITIES OF THE ALLYL$^+$/F$^-$ AND ALLYL$^-$/Li$^+$ ION PAIRS IN POLAR MEDIA*

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ABSTRACT

The relative thermodynamic stabilities of several ion-pair structures, including intimate and solvent-separated forms, in solution have been studied for the allyl$^+$/F$^-$ and allyl$^-$/Li$^+$ model systems. The electrostatic part of the solvent effects was modelled through the self-consistent reaction field (SCRF) theory and an extension of it including desolvation effects (SCRF/D theory).

Specific solvent effects were also analysed by explicitly incorporating a solvent molecule, via the supermolecule (SM) approach. It is shown that a more complete thermodynamic description of these systems is attained by using mixed continuum–SM schemes. This last approach allows qualitative separation of the individual contributions of the electrostatic and hydrogen-bonding effects, which are particularly relevant to a discussion of the relative stabilities of intimate and solvent-separated ion pairs in these systems.

INTRODUCTION

The discovery that ion pairs can play an important role in solvolytic reactions is one of the most important developments of modern physical organic chemistry [1–4]. In spite of the formidable experimental work done and advances made in this field, the structure of ion pairs appears to have received little attention from the quantum-chemical point of view. Among the few theoretical works reported up to now, we may mention some studies dealing with the electronic structure of ion pairs, including the discussion of several important bonding concepts [5,6].

However, it has been already recognized that the solvent may influence the stability of the ion pair decisively [6,7]. Solvent effects have been preferentially introduced via the well known supermolecule (SM) method, were a finite

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number of solvent molecules are explicitly incorporated in the quantum-chemical calculation.

Recently, a continuum-like model of electrostatic solvent effects, which introduces desolvation contributions, has been reported [8,9]. The application of this model, within a mixed discrete-continuum representation of environmental effects upon the thermodynamic stability of ion pairs in solution, has been found to be a useful tool for the theoretical study of ion-pair–solvent interactions [10,11]. The major advantage of the mixed discrete-continuum model is that it permits one to perform, in a rather simple way, a comparative study between the different types of ion-pair structures proposed by experimental chemists (intimate and solvent-separated ion pairs) [1].

This work presents an analysis of the free-energy profiles (FEP) for the interaction of allyl$^-$/Li$^+$ and allyl$^+$/F$^-$ ion pairs in vacuum, and in the presence of a strongly polarizable medium. Specific interactions with the solvent are also included to discuss the relative stability between the distinct types of (intimate and solvent separated) ion pairs present in these systems.

The choice of these model systems has been dictated by the fact that the allylic functionality appears to be involved, as an active site, in a significant number of solvolytic reactions [12].

Finally, some words concerning the type of wavefunctions and molecular geometries used in this work are due. First, since emphasis is placed not on the absolute magnitudes of the calculated total energies but rather on the qualitative trend, the CNDO/2 method seems to be appropriate for this purpose. An illustrative example of this argument is the study made previously on the allylfluoride ion pair reported by Bernardi et al. [6], where INDO and ab initio (STO-4G) calculations provided results that agreed very closely and were also in good qualitative agreement with experimental findings. Secondly, previous calculations of the FEP including solvent effects in related systems showed that the shape of the FEP of the potential curves are not appreciably affected by a moderate change in the fixed geometrical parameters [11]. Therefore, a comparative study in related systems, using standard geometries, may be done successfully without approaching the absolute minimum of the free-energy surface. Based on this argument, the inclusion of a large number of thermodynamically significant structures was considered instead of performing a full geometry optimization for each FEP of the several systems studied in this work. In summary, even though the methodology described above does not permit quantitative discussion of the relative thermodynamic stabilities of the ion-pair systems treated in this study, it allows a detailed description of the nature of the most relevant molecular interactions involved in these processes. Specifically, intrinsic vs. electrostatic and specific solvation contributions, as well as desolvation effects can be discussed.

METHOD AND MODELS

An outline of the SCRF-GBF and SCRF/D-GBF theories

Within the continuum approach to solvent-effects representation, the total free energy of the solute–solvent system is expressed as a function that depends parametrically on the macroscopic dielectric constant of the medium, ϵ, as

$$A(\epsilon) = E(1) + \delta A_S(\epsilon) \tag{1}$$

where $E(1)$ is the total energy of the isolated solute and $\delta A_S(\epsilon)$ is the free energy of solvation. A simple approximation for the quantity $\delta A_S(\epsilon)$ is the generalized Born formula (GBF) which leads after a variational treatment that minimizes the total free energy of the solute–solvent system $A(\epsilon,P)$ to the effective Fock operator [9–11]

$$\mathcal{F}(\epsilon,\mathbf{P}) = \mathcal{F}(1,\mathbf{P}) + \mathbf{V}_R(\epsilon,\mathbf{P}) \tag{2}$$

where $\mathcal{F}(1,\mathbf{P})$ is the standard Fock operator of the isolated solute and $\mathscr{V}_R(\epsilon,\mathbf{P})$, is the reaction field potential operator which, within the CNDO/2 approximation, is written as [8–11]

$$\mathscr{V}_R(\epsilon,\mathbf{P}) = -[1-1/\epsilon]\sum_B Q_B(\mathbf{P})\tau_{AB} \tag{3}$$

for each atomic centre A. The term $Q_B(\mathbf{P})$ is the net charge associated with atomic centre B, defined in terms of the one-particle density matrix $\mathbf{P}$, and τ_{AB} is the Coulomb integral representing the solute–solvent interaction potential.

The theoretical framework described by eqns. (1)–(3) is hereafter called the SCRF-GBF model of electrostatic solvent effects.

The model described above has provided a reasonably good description of solvation properties [13,14]. However, its application to the calculation of even elementary reaction paths of processes involving ion-pair formation requires a certain adaptation, in order to take into account desolvation effects.

We have recently proposed an extension of the SCRF-GBF formalism which continuously describes the desolvation step [10]. The correction to the GBF entails the following expression for the solvation free energy:

$$\delta A_S(\epsilon,\mathbf{P}) = -\tfrac{1}{2}[1-1/\epsilon]\sum_A \sum_B Q_A Q_B[1-F_{AB}]\tau_{AB} \tag{4}$$

where F_{AB} (S_{AB}) is a function of the overlap integral defined for each atomic pair A and B.

The theoretical scheme is then completed by minimizing $A(\epsilon,\mathbf{P})$, and the effective Fock operator obtained is similar to that given in eqn. (2), but where $\mathscr{V}_R(\epsilon,\mathbf{P})$ in eqn. (3) is replaced by

$$\mathscr{V}_R(\epsilon,\mathbf{P}) = -[1-1/\epsilon]\sum_B Q_B[1-\mathscr{F}_{AB}]\tau_{AB} \tag{5}$$

for each atomic centre A.

The theoretical framework summarized by eqns. (4) and (5) is hereafter called the SCRF/D-GBF model of electrostatic solvent effects.

RESULTS AND DISCUSSION

The allyl$^+$/F$^-$ and allyl$^-$/Li$^+$ systems

The first model systems analysed in this work were the allyl$^+$/F$^-$ and allyl$^-$/Li$^+$ ion pairs in the absence of a specific interaction with the solvent, CNDO/2 calculations of the relative energies of the symmetrical and unsymmetrical ion pairs were performed. The structural models considered are shown in Fig. 1. The geometry of the allyl framework was computed by reference to standard bond lengths and bond angles [15]. The reaction coordinate for the ion-pair formation process was defined as the distance R between the counterion ($P = F^-$ or Li^+) and the allylic frame (see Fig. 1).

Structure I represents an ion pair in which the counterion P approaches the central carbon of the allyl framework, above the plane of the molecule. Structure II corresponds to an ion pair in which the counterion P approaches the terminal carbon (C1 or C3) of the allyl group also above the plane of the allyl framework. Other structures with the counterion approaching the allyl group within the plane of the molecular system appeared to be largely unstable with respect to structures I and II and are not included here. The free-energy variations for both systems considered are displayed in Fig. 2–4.

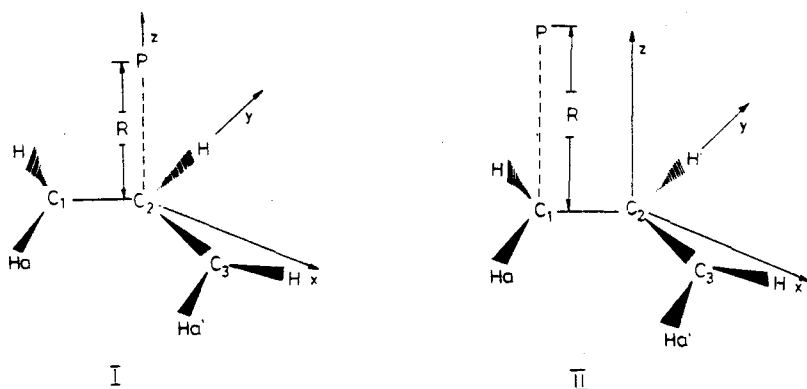Figure 2 shows the free-energy profile for the allyl$^-$/Li$^+$ system in the gas

Fig. 1. Structures considered for the calculation of the free-energy profiles for the allyl-fluoride and allyl-lithium systems.
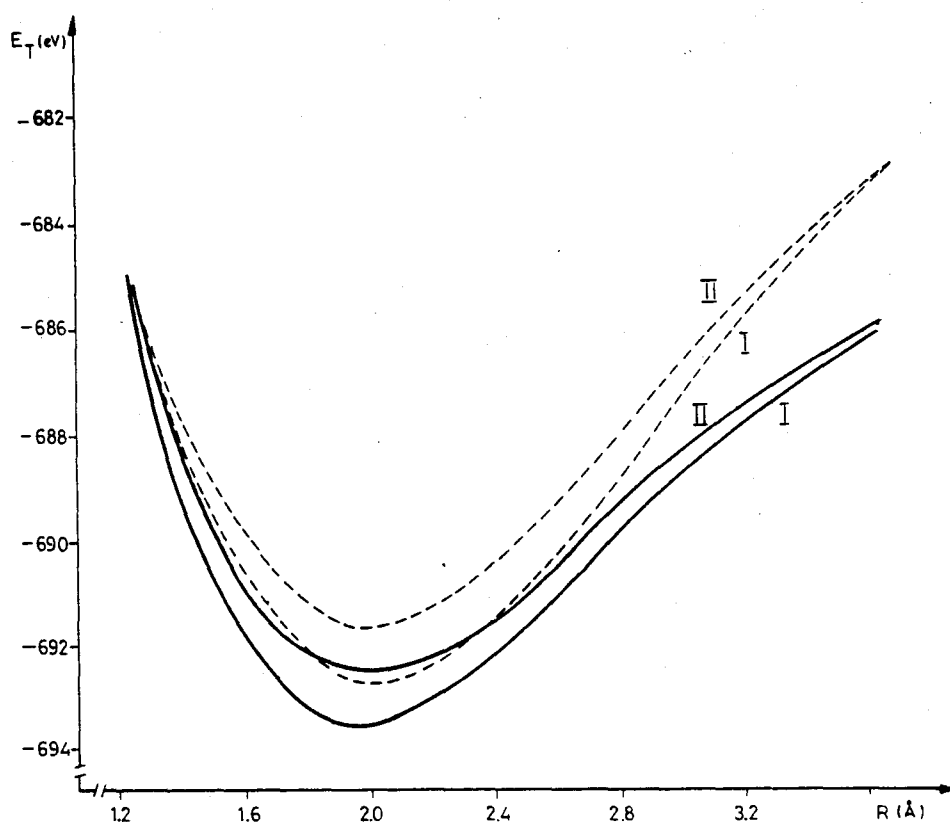
Fig. 2. The FEP for the allyl–lithium system calculated using the SCRF-GBF model: (---) in vacuum ($\epsilon = 1.0$); (—) in solution ($\epsilon = 80.0$).

phase and in the presence of a strongly polarizable medium (i.e. $\epsilon = 80$), using the SCRF-GBF model. The following results are relevant: (i) gas-phase calculations reveal a relative stability order I > II; (ii) the introduction of electrostatic solvent effects does not change the shape of the free-energy profiles and a trivial stabilization in an amount equal to the solvation energy of the corresponding complexes is observed; and (iii) calculations including desolvation effects showed no significant differences compared with the standard SCRF-GBF model. Accordingly, these data are not included in Fig. 2. It seems that desolvation effects do not introduce significant changes in the free-energy profiles of structures I and II. A possible explanation of this feature could be related to the strong electrostatic nature of the complexes formed, which manifests itself at distances where overlap is not very significant.

Figure 3 summarizes the free-energy changes in the gas phase and in solution using the SCRF-GBF model, for the allyl$^+$/F$^-$ system. Overall, the most stable complex in the case of the allyl$^+$/F$^-$ system seems to be the unsymmetrical
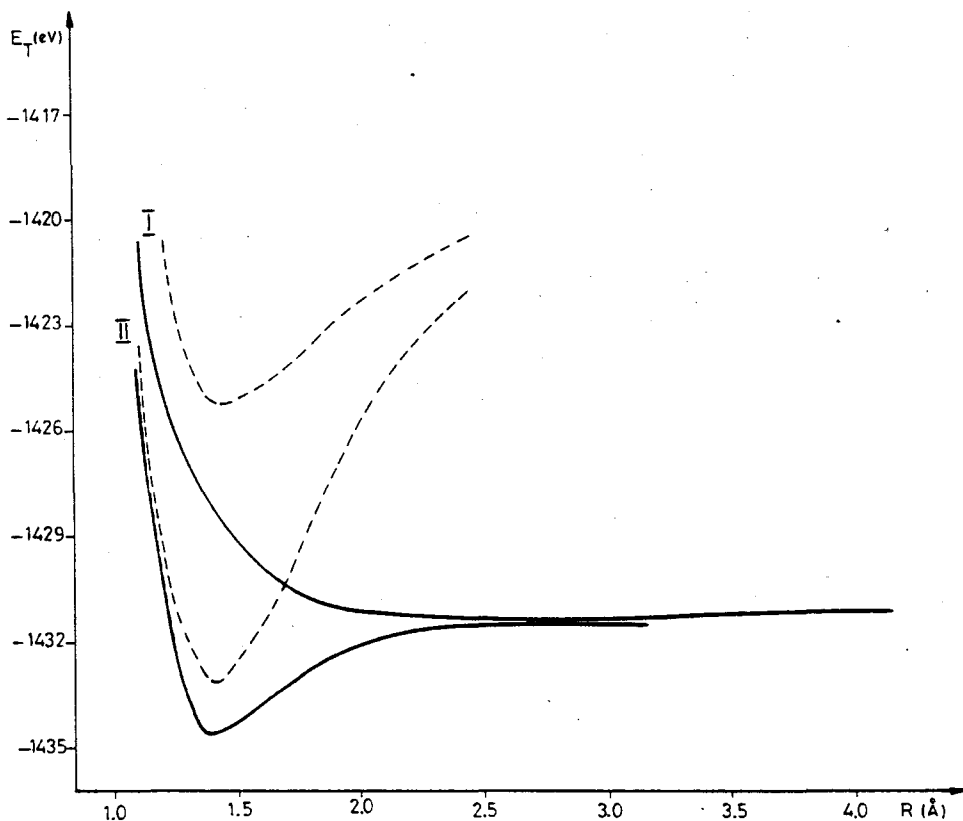
Fig. 3. The FEP for the allyl–fluoride system calculated using the SCRF-GBF model: (---) in vacuum; (—) in solution.

complex (structure **II**). This complex is characterized by a $d(\text{C–F})$ of distance 1.4 Å. The most relevant aspect of the solution FEP is that the strong solvation energy displayed by the symmetric complex (structure **I**) entails the preferential stabilization of the free-ion state. This result is consistent with the strong ionic character of this complex, compared with the unsymmetrical structure **II**, which has been found to show a significant amount of covalent character [6].

In summary, the main difference obtained after comparing the allyl$^-$/Li$^+$ and allyl$^+$/F$^-$ systems is that in the lithium complex the optimum interaction corresponds to a symmetrical structure, whereas in the allyl–fluoride system the most stable situation corresponds to an unsymmetrical ion pair. As a result, the lithium ion pair is stabilized at longer distances than in the fluoride complex and, therefore, desolvation effects are not very significant in the allyl–lithium system.

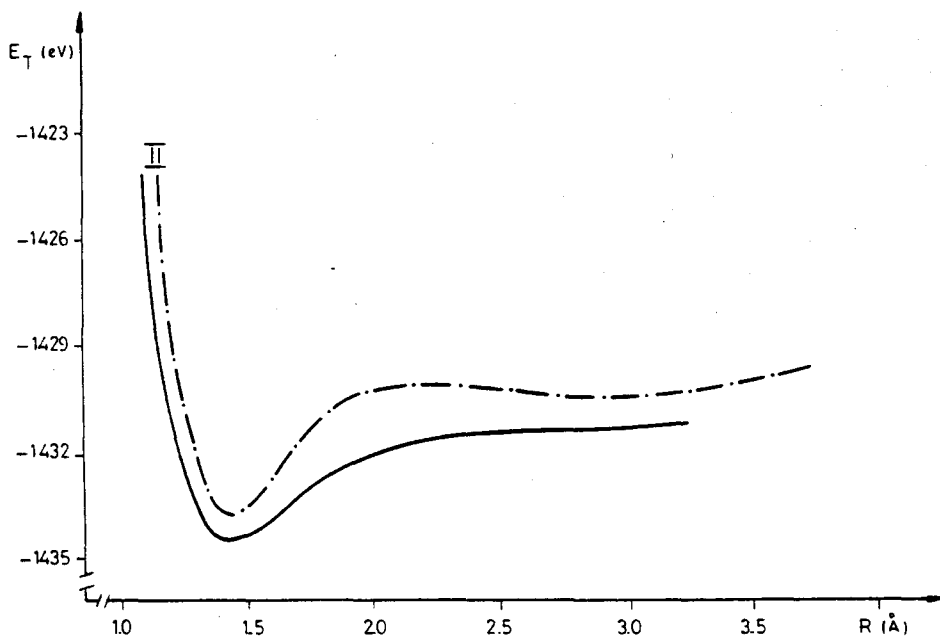Figure 4 summarizes the comparison between the solution-phase calcula-

Fig. 4. The FEP in solution for the allyl–fluoride system, structure II: (——) SCRF-GBF; (—·—·—) SCRF/D-GBF.

tions using the SCRF-GBF and SCRF/GBF models for the allyl$^+$/F$^-$ system. The comparison was made for the most stable structure (**II**). It may be seen that consideration of desolvation effects results in a double-well free-energy profile. The first minimum is located in the region $2.5 < R < 3.5$ Å. The flat shape of the SCRF/D curve reveals the major role that the electrostatic interactions play in the ion pair structure. The second minimum is characterized by $d(C-F) = 1.4$ Å, and the population analysis suggests a significant covalent component in the interaction present in this complex. This last result is in close agreement with previous semiempirical and ab initio calculations reported by Bernardi et al. [6] for this system. The desolvation barrier separating both minima was estimated to be about 7.5 kcal mol^{-1}.

Introduction of specific interactions with the solvent

In order to test the reliability of the SM approach for the description of ion pairs in solution, a solvent molecule (water in the present case) was explicitly included. The first step in this study was the calculation of the hydration energy, by one water molecule, of the free ions in the gas phase. Formally, the expression "hydration energy" is incorrect, since we did not include the actual
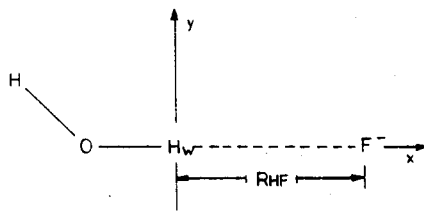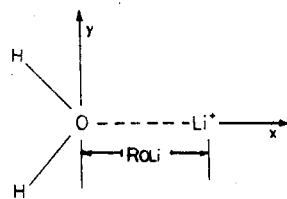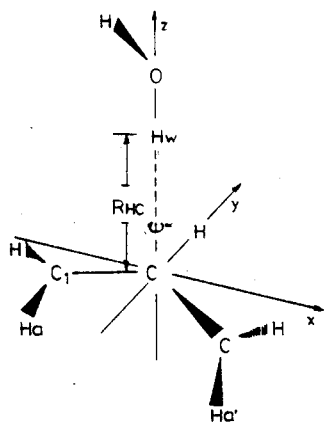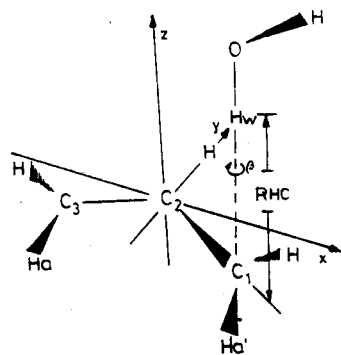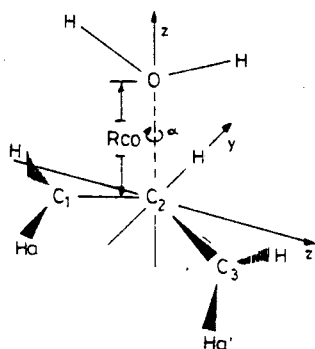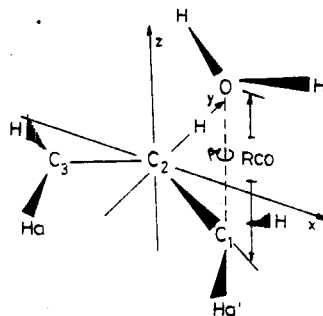
Fig. 5. Structures considered for the calculation of E_{wa} for cations and anions.

TABLE 1

Hydration energy by one water molecule for the cations and anions under study

Ion		R^a (Å)	Angle (°)	E_{wa} (kcal mol^{-1})
Allyl$^+$	(VIIIb)	1.4	$\beta = \pi/2$	-132.9
Allyl$^-$	(VIb)	1.6	$\beta = \pi$	-21.7
Li$^+$	(IV)	2.4	–	-44.7
F$^-$	(III)	1.2	–	-55.3

^{a}These geometrical parameters correspond to the optimized value.

coordination number of the solvent molecules for each ion. A more consistent notation for this calculation is "a water molecule affinity", E_{wa}.

Figure 5 summarizes the different hydration complexes for the cations and anions considered in this calculation. The geometries of these complexes were optimized with respect to the intermolecular distance R and the angles defining the orientation of the water molecule in the case of the allyl$^+$ cation.

The E_{wa} results are summarized in Table 1. It may be seen that in the case of the allyl$^+$/F$^-$ system, E_{wa}(allyl$^+$) $> E_{wa}$(F$^-$), in absolute value. This result suggests that, on the basis of SM calculation alone, the attack of the F$^-$ occurs on the already hydrated allyl$^+$ substrate, generating a solvent-separated ion pair (SSIP). Based on the free-ion state water affinity calculation, one would expect the SSIP form to be more stable than the corresponding intimate ion pair (IIP) complex. However, an SM calculation alone, in the absence of electrostatic solvation, showed the IIP form to be the more stable one. A decisive conclusion about the relative stability may then only be attained after a mixed continuum–SM calculation.

In the case of the allyl$^-$/Li$^+$ ion pair, E_{wa}(Li$^+$) $> E_{wa}$(allyl$^-$) in absolute value (Table 1). In other words, the SM calculation alone predicts the attack of the $[Li \cdots H_2O]^+$ species on the allyl$^-$ substrate. In this case, the preferential stabilization of an IIP or a SSIP would depend on the orientation of the hydrated Li$^+$ when it approaches the allyl$^-$ frame.

Relative stabilities of the IIP and SSIP

In order to test the quality of the predictions made for the preferential formation of IIP or SSIP in the systems under study, further calculations were performed from the E_{wa} results, using a mixed continuum–SM model. The continuum part accounting for electrostatic solvent effects was done using both SCRF and SCRF/D models. In addition, this calculation is of interest since it allows the separation of specific solvation effects (like hydrogen bonding) from those of purely electrostatic nature, and desolvation effects as well.

Figure 6 displays the different structures considered in the calculation of the reaction path for the formation of IIP in both allylic systems. Structures **IX** and **X** represent the attack of the $[Li \cdots H_2O]^+$ ion on the allyl$^-$ substrate. The reaction coordinate is defined in this case as the intermolecular R_{C-Li} distance. The approach is forced to occur with the orientation required to form a IIP.

Structures **XI** and **XII** define the corresponding IIP for the allyl$^+$/F$^-$ system. In this case, the attack of the $[F \cdots H_2O]^-$ ion is forced to occur along the two sites of the allyl$^+$ system shown in Fig. 6.

A first relevant result obtained from the calculation of the free-energy profile for the formation of the IIP is that the orientation of the water molecule ex-
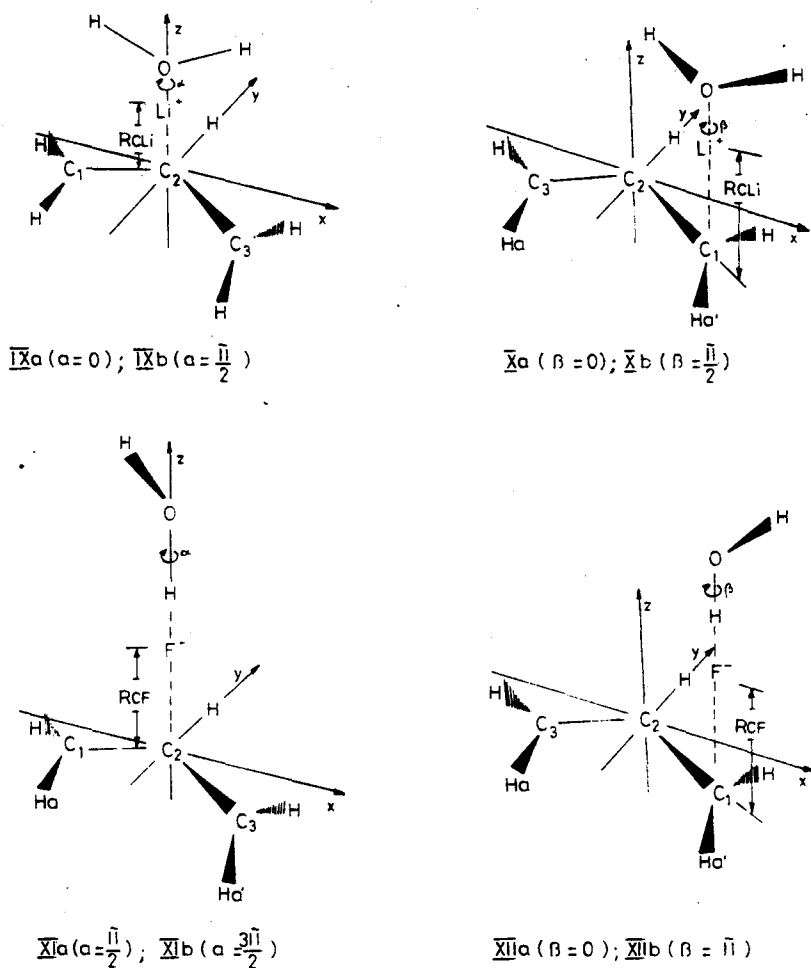

Fig. 6. Structures considered for the calculation of the FEP of the IIP complexes.
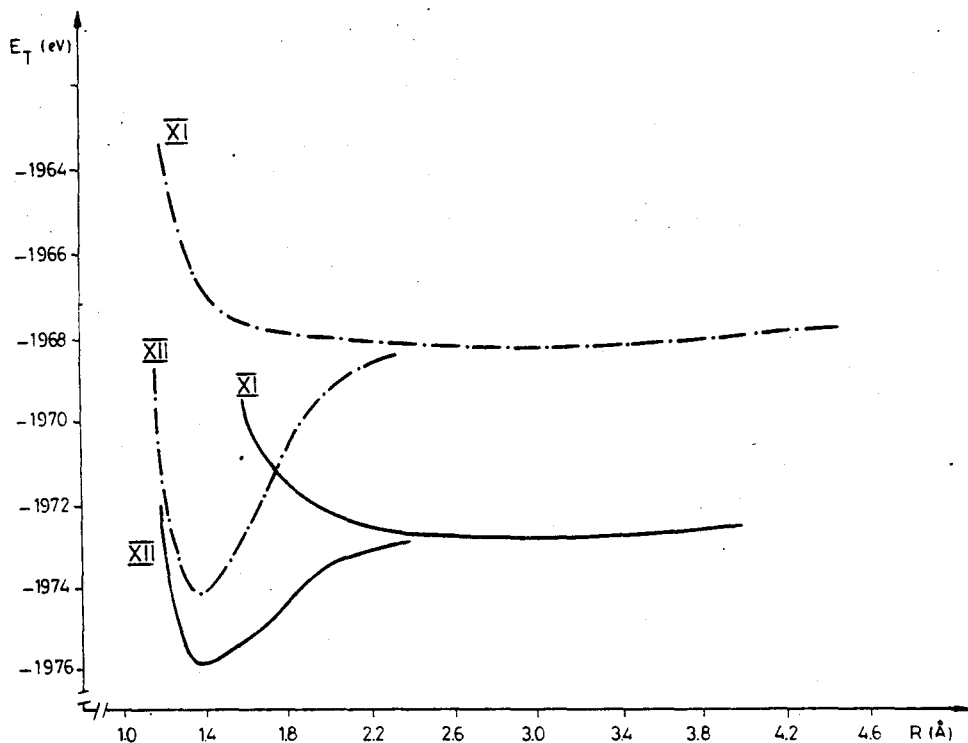
Fig. 7. FEP for the intimate ion pair in the allyl–fluoride system: (—) SM-SCRF, (---) SM-SCRF/D.

ternally coordinated to the ion pair has no significant effects on the free-energy variations of the solute–solvent system.

The results of the calculation on allyl–lithium including a water molecule do not show significant differences as compared with the calculations involving continuum solvent effects only. After the analysis of the four series of calculations discussed above, the E_{wa} calculation correctly predicts the preferential stabilization of the IIP with respect to the corresponding SSIP in this system.

Therefore, taking into account these results, the desolvation effects were analysed only for the most thermodynamically stable unsymmetrical complex in the allyl–fluoride system. The FEPs obtained with the mixed model, using the SCRF and SCRF/D methods are displayed in Fig. 7. The FEPs corresponding to structure **XI** are also included in the figure in order to provide a reference for the free-ion states in solution.

Useful information about this system may be obtained by comparing Figs. 7 and 4. This comparison allows a qualitative picture to be obtained of the effect of specific solvation on the stability of the IIPs for the allyl$^+$/F$^-$ system. It may be seen that while the continuum SCRF/D model predicts a double-well

$\underline{XIII}a\;(\alpha=\frac{\tilde{\Pi}}{2})\;;\;\underline{XIII}b\;(\alpha=\frac{3\tilde{\Pi}}{2})$

$\underline{XIV}a\;(\beta=0)\;,\;\underline{XIV}b\;(\beta=\tilde{\Pi})$

$\underline{XV}a\;(\alpha=0)\;;\;\underline{XV}b\;(\alpha=\frac{\Pi}{2}$

$\underline{XV}c\;(\alpha=\tilde{\Pi})$

$\underline{XVI}a\;(\beta=0)\;;\underline{XVI}b\;(\beta=\frac{\tilde{\Pi}}{2})$

$\underline{XVI}c\;\;(\beta=\tilde{\Pi})\;;\;\underline{XVI}d\;(\beta=\frac{3\tilde{\Pi}}{2})$
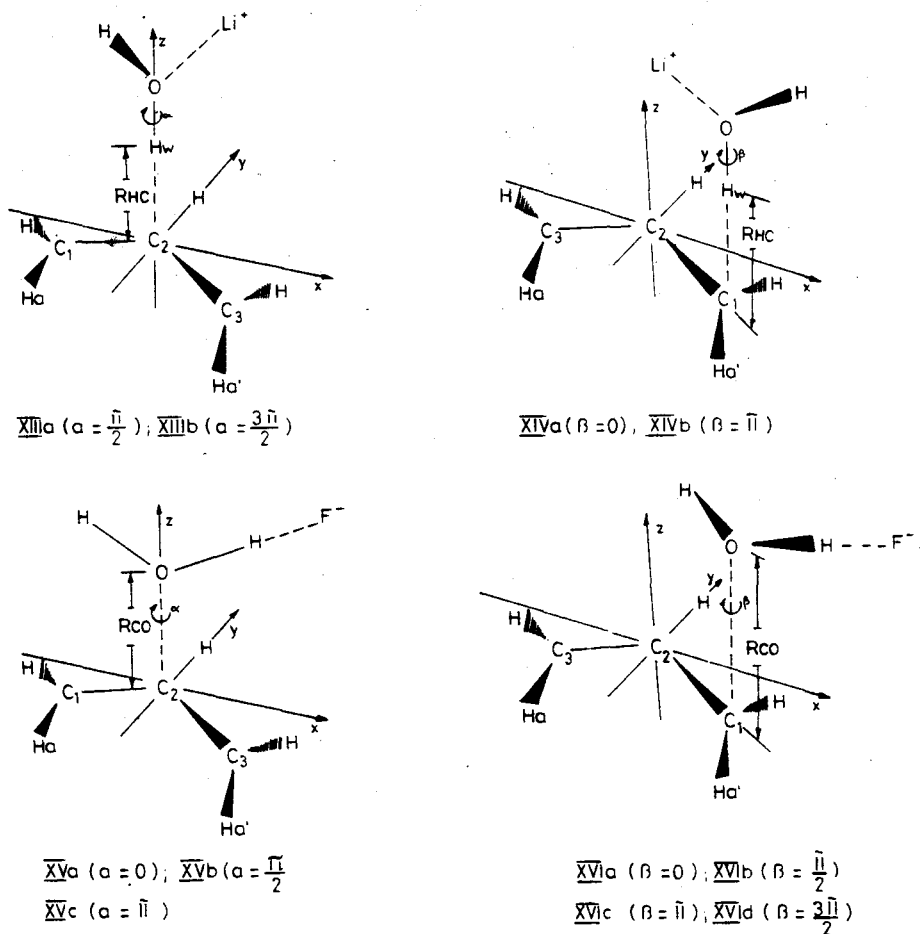
Fig. 8. Structures considered for the calculation of the solvent-separated forms of the allyl–lithium and allyl–fluoride ion pairs.

FEP for this system, the mixed predicts a one-minimum FEP in solution. The change of shape of the FEP by incorporating a water molecule may be attributed to the additional stabilization of the externally hydrated ion pair by the hydrogen-bonding contribution $F^-\cdots H_2O$.

Perhaps the most interesting aspect of the inclusion of specific solvation in the systems studied here is related to the possibility of analysing the relative stability of IIP and SSIP. With this feature in mind, we undertook a series of calculations involving the solvent-separated ion-pair structures displayed in Fig. 8. The most relevant results obtained may be summarized as follows.

(i) In the preferential stabilization of an IIP in the allyl–lithium system, two opposite effects operate. On one band, the specific interaction with a sol-

vent molecule favours the preferential stabilization of the intimate form. This result may be explained on the basis of E_{wa} values shown in Table 1. For instance, the formation of the IIP results from the attack of the hydrated Li^+ ion on the allylic substrate, whereas in the formation of the corresponding SSIP, the hydration preceding the ionic association would be expected to occur in the opposite direction. Since from Table 1 $E_{wa}(Li^+) > E_{wa}(allyl^-)$, we may conclude that the preferential stability of the IIP complex with respect to the corresponding SSIP is strongly related to the gas phase water affinity of the counterions. On the other hand, the "bulk" electrostatic effect of the solvent is stronger in the case of the SSIP complex, which displays a higher solvation energy. This effect may be explained on the basis of a greater charge separation displayed by the SSIP structure. Physically, this result is consistent with an increase in the actual dipole moment when passing from the IIP to the SSIP structures, which causes an increase in the electrostatic solute–solvent interaction in favour of the SSIP complex. Overall, the IIP complex appears to be more stable than the corresponding SSIP in the allyl–lithium system, indicating the relevance of specific solute–solvent interactions in this system.

(ii) In the allyl$^+$/F$^-$ system, the most stable ion pair is the one corresponding to an unsymmetrical SSIP. The electrostatic solvation entails the preferential stabilization of the SSIP by about 34.0 kcal mol^{-1} with respect to the corresponding IIP for this system. This result is in the close agreement with the results obtained after the E_{wa} calculation. This means that both electrostatic and specific interactions operate in favour of the preferential stabilization of the SSIP structure.

CONCLUDING REMARKS

The interaction of a number of different possible structures for the allyl$^+$/F$^-$ and allyl$^-$/Li$^+$ ion pairs in solution have been analysed. From the results obtained, the following conclusions may be drawn.

(i) Electrostatic solvation seems to play a relevant role in the stabilization of ion pairs by the interaction with the medium. Desolvation effects introduced within the continuum approach seem to be important in the case of short range interaction complexes (the allyl$^+$/F$^-$ system in the present case).

(ii) SM calculations predict the same trend in the relative-stability order of the different structures of the ion pairs considered here. Specific solute–solvent interactions permit the inclusion of IIP and SSIP complexes in the thermodynamic stability analysis presented here.

(iii) The mixed discrete-continuum model seems to be the most complete one in terms of the discussion of the different IIP and SSIP stabilities. Its major advantages is that it allows the separation of specific and "bulk" solvent-effect contributions.

In conclusion, it is expected that the mixed representation scheme of sol-

vation may be applied successfully to the qualitative understanding of solvation effects in ion-pair formation.

ACKNOWLEDGEMENTS

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