carbinol carbon (Figure 6), where each also has the most stable arrangement about the remaining carbon–carbon bond. Fortunately, the major contribution to differences between conformers appears to be restricted to γ substituents and thus each bond can be considered an isolated system.

With the populations of X, Y, and Z as x, y, and z, there are two equations that must simultaneously fit the observed spectral shift-of-shifts in addition to that implicit in the assumption that these three conformations represent the total of those under observation (the shift-to-shift effects used are from Figure 2):

$$x + y + z = 1.0$$

$$(-5.9)x + (-8.85)y + (-3.8)z = -5.5 = 24.5 - 19.0 \qquad \text{(C-1)}$$

$$(-8.85)x + (-3.8)y + (-5.9)z = -7.1 = 24.5 - 17.4 \qquad \text{(C-6)}$$

Simultaneous solution of these equations leads to a predicted ratio of conformers (x, y, and z, below) quite close to that predicted by MM-2 calculations.

	x		y		z
MM-2 ratio	42	:	13	:	44
NMR ratio	50	:	12	:	38

To arrive at a unique solution to the appropriate simultaneous equations, the number of observed shifts of carbons that vary with conformation must be equal to or greater than the number of distinct conformations minus one (the additional equation being provided by the identity that the sum of all conformer populations must equal 1), but in practice quite useful information can be obtained by a "local" analysis similar to that carried out above. It should be pointed out that this type of analysis can result in substantial errors in population percentages as our average shift prediction error (0.5) represents a significant fraction of the shift difference between anti and gauche relationships for both oxygen (Δ 5.2) and carbon (Δ 3.2) substituents. While this relatively soft fit excludes the possibility of obtaining precise, relative energies for various conformers, the qualitative results from such a direct solution determination rival those obtained from extrapolation of gas-phase observations that are carried out by molecular mechanics calculations. Certainly, these results confirm the quantitative relationship between shift effect and spatial orientation of γ substituents and provide ample justification for the application of the shift effect values used here for the experimental determination of conformational populations in appropriately substituted systems.

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Relaxation or Fluctuation of the Ionic Atmosphere in Charge-Transfer Reactions. An ab Initio Study of the Charge Transfer in the $(H_3O_2)^-$ and $(FCH_3F)^-$ Systems

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Abstract: To discuss the intervention of the ionic atmosphere on charge-transfer reactions, ab initio calculations have been carried out on the proton-transfer reaction in the $(H_3O_2)^-$ system, and on the fluoride-exchange reaction in the $(FCH_3F)^-$ system. In a simplified model, no solvent molecules have been considered, and a very limited number of neighboring ions have been taken. Li^+ and H^+ cations and the positive charge have been chosen as counterions. It has been found that counterion parameters belong to the reaction coordinate, so that fluctuations of counterions may induce the chemical process. An insight to these energetic results is made from the changes in charge density produced by neighboring ions. The main conclusion is that external perturbations to the chemical system have the same effect as variations in the internal coordinates of the system, thus showing that the concept of reaction coordinate is wider than usually thought.

At present, most theoretical studies on chemical reactivity deal with isolated systems. Although a few new methods like flowing-afterglow[1] and techniques like ion cyclotronic resonance[2] allow the study of reactions at very low pressures, nearly all experimental studies are carried out in a condensed medium. Actually, experimental work is usually done in solution, where environmental effects are quite important. These effects are due simultaneously to the solvent and the ionic atmosphere. The influence of solvent on chemical reactions already has been studied in a large number of cases. However, the effect due to the presence of neighboring ions has been investigated far less. The study of this last effect is the ultimate goal of the present paper.

Let us summarize first the various models of the solvent, since there is an analogy with the different ways of representing the ionic atmosphere. The solvent effect on chemical reactions has been extensively studied within the framework of transition-state theory.[3,4] The first studies of Debye[5] and Onsager,[6] which used a continuum model for the solvent, have been recently improved by Jørgensen[7-10] by means of a Monte Carlo study. In these static approaches, the solvent is supposed to be in equilibrium with the chemical system by a relaxation that follows the chemical process. Studies of the dynamical effect of the solvent were introduced by Kramers[11] in 1940, and have been widely developed by Hynes[12,13] using a generalized Langevin equation. In this stochastic

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(1) Bourie, J. H. *Acc. Chem. Res.* **1980**, *13*, 76.

(2) Ferguson, E. E.; Fehsenfeld, F. C.; Schneltekpt, A. L. *Adv. At. Mol. Phys.* **1969**, *5*, 1.

(3) Glasstone, S.; Laidler, K. J.; Eyring, H. *The Theory of Rate Processes*; McGraw-Hill: New York, 1941.

(4) Evans, M. G.; Polanyi, M. *Trans. Faraday Soc.* **1931**, *31*, 875.

(5) Debye, P. *Trans. Electrochem. Soc.* **1942**, *82*, 265.

(6) Onsager, L. *Phys. Rev.* **1938**, *54*, 554.

(7) Chandrasekhan, J.; Smith, S. F.; Jørgensen, W. L. *J. Am. Chem. Soc.* **1984**, *106*, 3049.

(8) Chandrasekhan, J.; Smith, S. F.; Jørgensen, W. L. *J. Am. Chem. Soc.* **1985**, *107*, 154.

(9) Chandrasekhan, J.; Jørgensen, W. L. *J. Am. Chem. Soc.* **1985**, *107*, 2974.

(10) Madura, J. D.; Jørgensen, W. L. *J. Am. Chem. Soc.* **1986**, *108*, 2517.

(11) Kramers, H. A. *Physica (The Hague)* **1940**, *7*, 284.

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treatment, solvent intervention is taken into account in the friction coefficient. A more explicit way of intervention of solvent parameters can be included, as we have done in several cases, by using a limited number of solvent molecules.[14-16] We showed that solvent motion is correlated with the movement of the chemical system along the reaction coordinate, in such a way that fluctuations of solvent molecules may induce the chemical process. This feature has been emphasized recently by Hynes[17,18] in a dynamical study of an S_N2 reaction, where he finds that the molecular dynamics is strongly dependent on the instantaneous local configuration of the solvent at the transition state.

The effect due to neighboring ions has been far less studied. To our knowledge, the first work on this subject was the study of the effect of the ionic atmosphere on chemical reactions by Marcus[19] in 1965, where he showed that some amount of activation free energy in outer-sphere electron-transfer processes arises from reorganization of the ionic atmosphere. In this study, the latter is treated as a continuum, and the variation in free energy due to its reorganization turns out to be much smaller than the change due to reorganization of the solvent. More recent theoretical studies[20,21] have not really included the effect of the ionic atmosphere, but one or two ions only have been considered within a discrete representation. This simplification allows one to perform ab initio calculations, not possible otherwise if several ions and solvent molecules ought to be considered together. It is obvious, as pointed out by Marcus, that there is a reorganization of the ionic atmosphere along a chemical reaction. In the aforementioned studies, one cannot think of an ionic atmosphere, not only because a small number of ions have been considered and solvent effect has been neglected, but also because ion motions during chemical system evolution have not been allowed. In analogy to the ideas stated in the preceding paragraph on solvent effect, one can consider either a static effect of the ionic atmosphere tied to its relaxation, or a more dynamic effect on the chemical system due to its fluctuation. In the present paper, our aim is to analyze the influence of neighboring ions on a chemical reaction, without taking into account the solvent effect, but allowing neighboring ions motions in order to study their intervention in the chemical process.

To reach this goal, we focus our attention on charge-transfer reactions, where the influence of neighboring ion parameters is expected to be especially important. Two examples are chosen for this purpose: the proton transfer in the $(H_3O_2)^-$ system and the fluoride exchange in the S_N2 reaction $FCH_3 + F^- \rightarrow F^- + H_3CF$.

The results of the present paper are divided into two sections. First, the influence of neighboring ion parameters on the reaction coordinate is analyzed starting from energetic results. In the second section, changes in charge density generated by neighboring ions allow a deeper insight into the participation of their parameters in the chemical process.

Methodology

For small negatively charged systems like those studied in this paper, positive counterions were considered to be in intimate contact with the reacting system. In the present work, neighboring ions were modeled by a reduced number of cations: Li^+, H^+, and the positive charge as a general representation of a positive ion. Since we were interested in the intervention of counterion parameters in the reaction coordinate, we used the supermolecule model. This allowed us to employ commonplace methods to locate reactants and transition states in the full potential energy hypersurface. Closed-shell RHF energy calculations were performed by standard ab initio methods using the 3-21G[22] and 4-31G[23] basis set. The positive charge is represented by a hydrogen atom whose basis set is a lone Gaussian function with a very small exponent. The MONSTERGAUSS[24] and GAUSSIAN 82[25] series of programs were used for all computations.

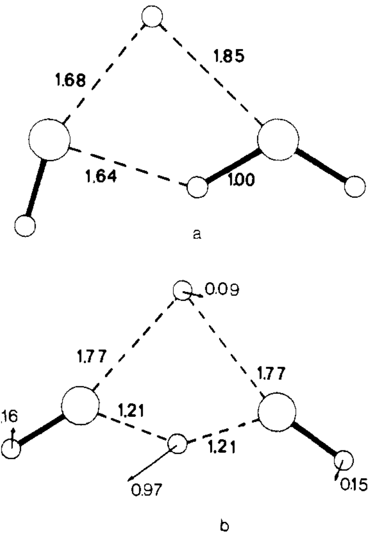

Figure 1. $(H_3O_2)^-{\cdot}Li^+$ system: (a) energetic minimum, (b) transition state and main components of transition vector expressed in Cartesian coordinates. Distances are given in angstroms and angles in degrees.

Energetic Results

(a) $(H_3O_2)^-$ System. The $(H_3O_2)^-$ system has been studied by several authors[26-32] through different levels of theory. Single-configuration calculations using the 3-21G basis set led to only a symmetric minimum,[26] whereas with the 4-31G basis set a double-well minimum was obtained.[16,27-32] Furthermore, an increase of the basis set size raises the barrier height for the proton transfer,[29-32] whereas introduction of the correlation energy lowers it.[29-32] Thus, monoconfigurational 4-31G calculations reproduce quite well higher level calculations, so they were used in all computations for this system.[29] Previous studies using the 4-31G basis set revealed that the barrier height which separates both asymmetric minima is 0.20 kcal/mol.[16,31]

The first representation we used as a counterion was the Li^+ cation. We present in Figure 1a the energetic minimum obtained by full optimization of the $(H_3O_2)^-{\cdot}Li^+$ system. One can see that the O–H–O bond is no longer linear, owing to the presence of the Li^+ cation, which is bonded simultaneously to both oxygen atoms. Further, the difference between the two Li–O distances must be stressed: the shorter Li–O distance is related to the longer O–H bond and vice versa. The transition state (Figure 1b) corresponds to a totally symmetric C_{2v} structure that lies 2.97 kcal/mol above

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(12) Hynes, J. T. *Annu. Rev. Phys. Chem.* **1985**, *36*, 573.

(13) (a) Grote, R. F.; Hynes, J. T. *J. Chem. Phys.* **1980**, *73*, 2715. (b) Grote, R. F.; Hynes, J. T. *Ibid.* **1981**, *74*, 4465.

(14) Jaume, J.; Lluch, J. M.; Oliva, A.; Bertrán, J. *Chem. Phys. Lett.* **1984**, *106*, 232.

(15) Muñiz, M. A.; Bertrán, J.; Andrés, J. L.; Duran, M.; Lledós, A. *J. Chem. Soc., Faraday Trans. 1* **1985**, *81*, 1547.

(16) Andrés, J. L.; Duran, M.; Lledós, A.; Bertrán, J. *Chem. Phys. Lett.* **1986**, *124*, 177.

(17) Bergsma, J. P.; Gertner, B. J.; Wilson, K. R.; Hynes, J. T. *J. Chem. Phys.*, in press.

(18) Bergsma, J. P.; Gertner, B. J.; Wilson, K. R.; Lee, S.; Hynes, J. T. *J. Chem. Phys.*, in press.

(19) Marcus, R. A. *J. Chem. Phys.* **1965**, *43*, 679.

(20) (a) Sanhueza, J. E.; Tapia, O. THEOCHEM **1982**, *89*, 131. (b) Rode, B. M. *Theor. Chim. Acta* **1980**, *56*, 245. (c) Černušák, I.; Urban, M. *Collect. Czech. Chem. Commun.* **1978**, *43*, 1956.

(21) (a) Scheiner, S.; Redfern, P.; Szczęśniak, M. M. *J. Phys. Chem.* **1985**, *89*, 262. (b) Szczęśniak, M. M.; Scheiner, S. *Ibid.* **1985**, *89*, 1835.

(22) Binkley, J. S.; Pople, J. A.; Hehre, W. J. *J. Am. Chem. Soc.* **1980**, *102*, 939.

(23) Ditchfield, R.; Hehre, W. J.; Pople, J. A. *J. Chem. Phys.* **1971**, *54*, 724.

(24) Peterson, M.; Poirier, R. Program MOSTERGAUSS, Department of Chemistry, University of Toronto.

(25) Binkley, J. S.; Frisch, M. J.; DeFrees, D. J.; Krishnan, R.; Whiteside, R. A.; Schlegel, H. B.; Fulder, E. M.; Pople, J. A. GAUSSIAN 82, Carnegie-Mellon University, Pittsburgh, PA.

(26) Wolfe, S. *Can. J. Chem.* **1984**, *62*, 1465.

(27) Newton, M. D.; Ehrenson, S. *J. Am. Chem. Soc.* **1971**, *93*, 4971.

(28) Jørgensen, W. L.; Ibrahim, M. *J. Comput. Chem.* **1981**, *2*, 7.

(29) Hillebrand, E. A.; Scheiner, S. *J. Am. Chem. Soc.* **1984**, *106*, 6266.

(30) Szczęśniak M. M.; Scheiner, S. *J. Chem. Phys.* **1982**, *77*, 4586.

(31) Rohlfing, C. M.; Allen, L. C.; Cook, C. M.; Schlegel, H. B. *J. Chem. Phys.* **1983**, *78*, 2498.

(32) Frisch, M. J.; Del Bene, J. E.; Binkley, J. S.; Schaefer, H. F., unpublished results.

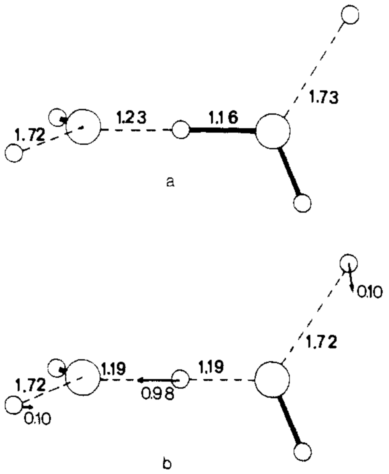

Figure 2. $(H_3O_2)^-\cdot 2Li^+$ system: (a) energetic minimum, (b) transition state and main components of transition vector expressed in Cartesian coordinates. Distances are given in angstroms and angles in degrees.

the two minima. In this structure there is an equidistance between the lithium and oxygen atoms. Hence, the Li^+ cation has already moved halfway toward the opposite asymmetric minimum. To analyze the importance of the Li^+ motion, the transition vector is also displayed in Figure 1b. It suggests that the main component corresponds to the central hydrogen, although other significant components involve the Li^+ cation and the remaining two hydrogens. This fact reveals that the last three atoms correlate their motion with the main motion of the process, that is, the proton transfer.

To check the importance of counterion motion in the chemical process, the Li–O bond distances in the structure of Figure 1a were switched and all the remaining geometrical parameters were allowed to relax. In this way, a spontaneous proton transfer was obtained. Thus, one can say that the proton accommodates its position to the counterion motion. The traditional sight that the counterion follows the chemical process by a relaxation must be complemented by the opposite view: a fluctuation of the counterion can induce the chemical process.

In the above study with only one counterion, a large distorsion of the $(H_3O_2)^-$ system arises due to the Li^+ cation (Figure 1a). In order to improve our theoretical model, a second study was performed with two Li^+ cations, each one of them attached to each negatively charged oxygen. In Figure 2a the fully optimized system $(H_3O_2)^-\cdot 2Li^+$ is presented. The structure obtained exhibits a linear O–H–O bond, and is far more symmetric than the $(H_3O_2)^-\cdot Li^+$ system (Figure 1a) and the gas-phase $(H_3O_2)^-$ system (1.09 and 1.37 Å for the two central O–H distances),[16] while the two Li–O distances have nearly the same length. The transition state, presented in Figure 2b, lies 0.01 kcal/mol above the minima, causing such a flat well that the proton can freely oscillate around its position in the minimum. However, the existence of a transition state with a low barrier still allows one to analyze its transition vector. The main components, depicted in Figure 2b, show that the fundamental motion corresponds to the proton transfer, although there are two significant components involving the Li^+ cations. Therefore, the motions of the lithium atoms and the central proton are correlated. One may say again that the proton adjusts its position to the fluctuations of the two Li^+ cations.

In order to extend the results obtained with the Li^+ cation, a positive charge is also used, as a simple representation of any positive ion. A first-order approximation for the effect of a positive charge can be obtained by plotting the molecular electrostatic potential (MEP) created around the $(H_3O_2)^-$ system. In this way, two minima are located, one at 1.03 Å near the hydroxyl fragment and another one at 1.05 Å near the water fragment. If a positive charge is placed at the first MEP minimum, and all geometrical parameters are relaxed, the positive charge approaches the negative oxygen until 1.00 Å, whereas the O–H–O bond becomes very asymmetric, such that the water molecule stays away at a distance of 1.71 Å. On the contrary, placement of a positive charge at the second MEP minimum not only causes the oxygen and the positive charge approach each other, but also promotes the spontaneous proton transfer to the other oxygen, so that a water molecule is formed at 1.71 Å from the hydroxyl fragment. Other sites have also been tested by placing the positive charge at several distances from the oxygen atom of the water fragment. All these cases cause the spontaneous proton transfer by full geometry optimization. This fact shows again that proton transfer is tied to fluctuations of the counterions. When two positive charges are used, each one placed at each MEP minimum, full geometry optimization leads to a symmetric structure, where the distances between the positive charges and the oxygens are 1.03 Å, and the distances between the central hydrogen and the oxygen atoms are 1.18 Å. This confirms the tendency noted in the previous example, where two Li^+ cations were attached to the $(H_3O_2)^-$ system.

Table I. Initial and Final Distances[a] for the Counterion–$(FCH_3F)^-$ System

Ⓐ---F—CH_3·····F^- Ⓐ---F^-·····CH_3—F

R_1 R_2 R_3 R_1 R_2' R_3'

Ⓐ	R_1	R_2	R_3	R_2'	R_3'
Li^+	1.66	1.45	2.31	2.59	1.41
H^+	0.96	1.45	2.31	2.70	1.40
⊕	1.07	1.45	2.31	2.57	1.41

[a] Distances in angstroms.

(b) $(FCH_3F)^-$ System. Theoretical results for the fluoride-exchange reaction have shown that the energetic profile is strongly dependent on the basis set being used.[14,33] These results indicate that the 3-21G basis set is the minimum level of theory for which a double-well energetic profile is obtained, in qualitative agreement with experimental data.[34,35] The potential barrier has been computed to be 12.2 kcal/mol relative to the double-well minima,[14] although the transition state is more stable than the reactants. Use of larger basis sets[36,37] raises the energy of the transition state over that of the reactants, in good agreement with experimental results.[34,35] In the present example, the size of the system to be studied prevented us from using extended basis sets. Therefore, we restricted ourselves to the 3-21G basis set, which has been shown to yield good qualitative results. The Li^+ cation and the positive charge have been used as counterions, as in the $(H_3O_2)^-$ species. For this system, the H^+ has also been used as a third example of a counterion to allow us to analyze the difference in behavior between the positive charge and the H^+.

When our model includes only one counterion, it can be placed in two ways. If it is placed near the F^- anion, the fluoride-exchange reaction is impeded. In reality, a contact ion pair is formed between the fluoride anion and the counterion, while a methyl fluoride molecule stays far away from it. A second way can be followed by placing the counterion in the vicinity of the fluorine bonded to the carbon atom. For Li^+ and H^+, the distance between the counterion and the fluorine atom has been chosen to be that obtained when the systems $Li^+\cdot FCH_3$ or $H^+\cdot FCH_3$ are fully optimized. For the positive charge, an analysis of the MEP plot generated along the F–C–F axis shows a minimum near the fluorine atom. The positive charge is placed at the location of this minimum when the $\oplus\cdot FCH_3\cdot F^-$ system is studied. When the counterion is placed near the fluorine bonded to the carbon atom, and full optimization of the $FCH_3\cdot F^-$ fragment is performed without a reoptimization of the counterion–fluorine distance, a fluoride exchange is spontaneously produced in all three cases (Table I). A contact ion pair is formed by the counterion and the fluorine formerly belonging to the methyl fluoride. At the

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(33) Dedieu, A.; Veillard, A. In *Quantum Theory of Chemistry Reactions*; Daudel, R., Pullman, A., Salem, L., Veillard, A., Eds.; Reidel: Dordrecht, 1980; Vol. 1, p 69.

(34) Bohme, D. K.; McKay, G. I.; Payzant, J. D. *J. Am. Chem. Soc.* **1974**, *96*, 4027.

(35) Olmstead, W. N.; Braumann, J. I. *J. Am. Chem. Soc.* **1977**, *99*, 4219.

(36) Dedieu, A.; Veillard, A. *J. Am. Chem. Soc.* **1972**, *94*, 6730.

(37) Duke, A. J.; Bader, R. W. F. *Chem. Phys. Lett.* **1971**, *10*, 631.

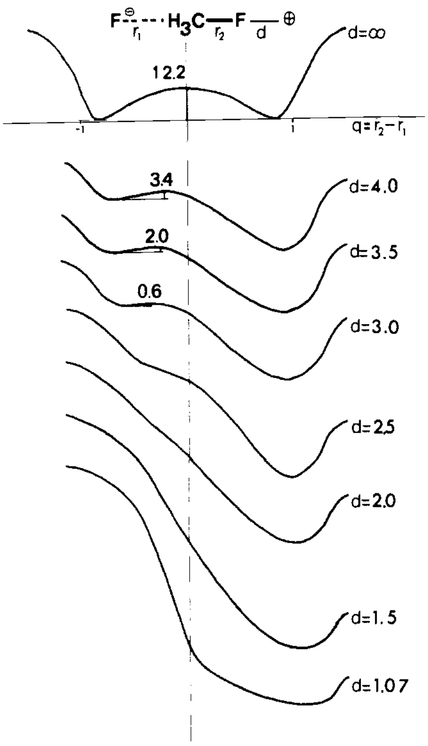

Figure 3. Energetic profiles for the ⊕·$(FCH_3F)^-$ system for several values of the positive charge–fluorine distance. Energies are given in kcal·mol^{-1} and distances in angstroms.

same time, a new methyl fluoride molecule is formed far off the ion pair. Thus, for this charge-transfer S_N2 reaction we obtain a result close to that of a proton-transfer process; an approach of the counterion to the fluorine atom bonded to carbon causes a spontaneous fluoride exchange, so that we can say that the methyl fragment adjusts its position to the fluctuations of the counterion.

In order to show more clearly how the counterion–fluorine distance intervenes in the reaction coordinate, we present in Figure 3 the energetic profile of the fluoride-exchange reaction for several values of the distance between the fluorine atom and the positive charge. The reaction coordinate q has been defined as the difference between the leaving fluorine–carbon and the entering fluorine–carbon distances. The shapes of the various profiles allow one to analyze the dependence of the potential energy surface on the counterion–fluorine distance. As shown earlier, at short distances the energetic profile decreases monotonically until the proton-transfer process is completed. At 3 Å and longer distances, a potential barrier separates the two asymmetric minima, ranging from 0.58 kcal/mol at 3 Å to 12.20 kcal/mol in the unperturbed (i.e., $d = \infty$) system. Besides this energetic result, other facts arise from this figure. The first minimum becomes less asymmetric with the decrease of the counterion–fluorine distance; on the contrary, the transition state is more advanced in the reaction coordinate, in good agreement with Hammond's principle. Further, the product is more asymmetric the shorter the counterion–fluorine distance. In other words, the energetic profile changes as a function of the counterion parameter values, so these parameters clearly belong to the reaction coordinate, and fluctuations of the counterion will affect the S_N2 chemical reaction.

As in the $(H_3O_2)^-$ system, our theoretical model can be improved by including two counterions, each one attached to each fluorine atom. As an example, we show in Figure 4a the intermediate of the $(FCH_3F)^-{\cdot}2Li^+$ system, and in Figure 4b the transition state for the fluoride-exchange reaction. The calculated potential energy barrier is 5.8 kcal/mol, which is lower than the barrier in the $(FCH_3F)^-$ system (12.20 kcal/mol). This corresponds to the same behavior of the $(H_3O_2)^-$ system where the presence of two counterions increased the symmetry of the system and lowered the barrier for the proton transfer.

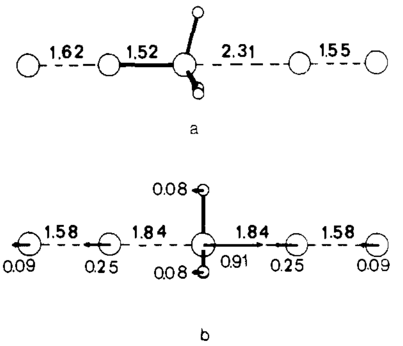

Figure 4. $(FCH_3F)^-{\cdot}2Li^+$ system: (a) energetic minimum, (b) transition state and main components of transition vector expressed in Cartesian coordinates. Distances are given in angstroms and angles in degrees.

Regarding the intervention of the counterion parameters in the reaction coordinate, we can see in Figure 4a that the two F–Li distances differ by 0.07 Å, and that these two distances must switch to reach the final product. This intervention in the reaction coordinate can be better understood by analyzing the transition vector depicted in Figure 4b. It shows clearly that the main components correspond to the change in the F–C distances, although other significant components correspond to the F–Li distance change. By extrapolation, one can affirm that there must be a contraction of the ionic atmosphere around the leaving fluoride, whereas there must be an expansion of the ionic atmosphere around the entering fluoride.

Charge Density Analysis

Chemical reactions are usually studied with potential energy hypersurfaces, where stationary points (minima and transition state) are located and the reaction barrier is computed and interpreted according to transition-state theory. The above studies have been carried out with this theory in mind. A different treatment is based in the topology of the total charge density in a given molecular system.[38] From the analysis of the charge density, bond critical points and bond paths can be defined.[39] The charge density at the bond critical points is related to the bond strength.[38] The network of bond paths defines in turn the molecuar graph of the system.[39] In this description, the concept of structure is not associated with a molecular geometry, but to an equivalence class of molecular graphs. A chemical reaction is a trajectory which must cross one boundary between two neighboring structural regions. These boundaries form the catastrophe set of the system.[40] With these ideas in mind, the analysis of the charge density generated by the external presence and fluctuations of counterions allows us to get a deeper insight into the intervention of the counterion parameters on the reaction coordinate.

(a) $(H_3O_2)^-$ System. In the energetic study, we have shown that the $(H_3O_2)^-{\cdot}Li^+$ system exhibits a nonlinear central O–H–O bond, and that the Li^+ cation is asymmetrically bonded to both oxygens. We have also shown that when the two Li–O distances are switched and the remainder of geometrical parameters is optimized, a spontaneous proton transfer is obtained. Figure 5a shows the charge density map of the energetic minimum of the $(H_3O_2)^-{\cdot}Li^+$ system (Figure 1a). Figure 5b corresponds to the same structure, where the two Li–O distance have been interchanged. Analysis of Figure 5a shows the formation of a cyclic structure, since a ring critical point with a low charge density appears (0.02). Bond critical points are also shown, along with the bond paths. One can see that the Li^+ cation is bonded more tightly to the hydroxylic oxygen (0.05) than to the water oxygen (0.03). The water molecule can also be observed, although the charge density at the inner bond critical point (0.28) is smaller

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(38) Bader, R. F. W.; Tal, Y.; Anderson, S. G.; Nguyen-Dang, T. T. *Isr. J. Chem.* **1980**, *19*, 8.

(39) Bader, R. F. W.; Anderson, S. G.; Duke, A. J. *J. Am. Chem. Soc.* **1979**, *101*, 1389.

(40) Bader, R. F. W.; Nguyen-Dang, T. T.; Tal, Y. *J. Chem. Phys.* **1979**, *70*, 4316.

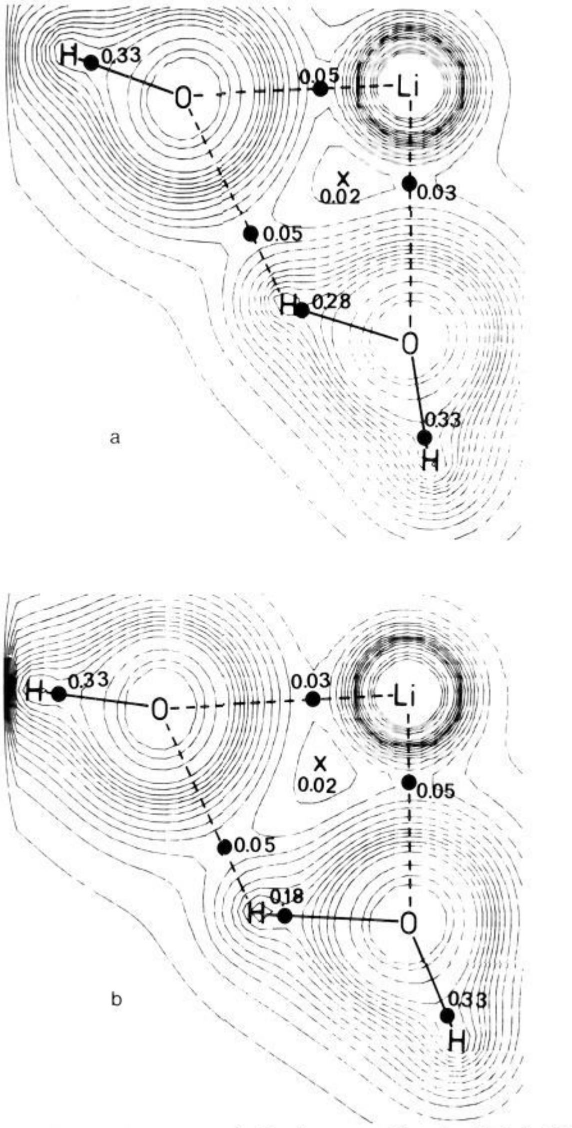

Figure 5. Charge density maps in the plane containing the $(H_3O_2)^-\cdot Li^+$ system (a) for the energetic minimum and (b) for the same structure with the two Li–O distances switched. ● indicates bond critical points, X indicates ring critical points, and numbers indicate charge density at these points. Bond paths linking atoms are also shown.

than the charge density at the outer bond critical point (0.33). This values reflect the distortion of the water fragment caused by the formation of the hydrogen bond.

When the Li–O distances are switched without relaxation of the remainder of geometrical parameters (Figure 5b), the values of the charge density at the Li–O bond critical points are also switched. The charge density at the hydrogen bond critical points (0.05) does not change. The main change is found at the water inner bond critical point, where the charge density is 0.18, down from 0.28. Therefore, the fluctuation of the counterion, which is external to the chemical system, has produced a noticeable decrease in the strength of the inner water O–H bond, thus facilitating the proton-transfer process. It must be emphasized that the effect produced by the external perturbation is the same as that which would have been produced by a strong distortion of the O–H bond. Such a strong distortion clearly corresponds to the reaction coordinate, so it can be understood that counterion parameters participate in the reaction coordinate.

(b) $(FCH_3F)^-$ System. In Figure 6 the charge density map of the FCH_3F^- system is presented. One of the methyl hydrogens is placed in the plane of the plot, whereas the remaining two hydrogens are situated out of the plane. The C–H bond critical point is easily detected, and the main bond critical points (a and b) are seen on the two C–F bond paths.

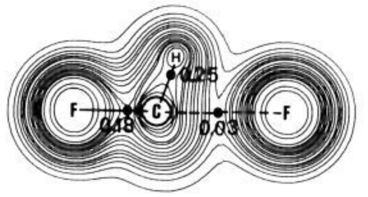

Figure 6. Charge density map in the plane containing the two fluorine atoms, the carbon, and one hydrogen of the methyl group for the $(FCH_3F)^-$ system. Conventions are like those in Figure 5.

Table II. Charge Density Values at the Two F–C Bond Critical Points *a* and *b*[a]

system	R	a	b
FCH_3F^-		0.182	0.032
$Li^+\cdot FCH_3F^-$	1.66	0.154	0.033
$H^+\cdot FCH_3F^-$	1.07	0.132	0.033
$\oplus\cdot FCH_3F^-$	1.07	0.141	0.033
$H^+\cdot FCH_3F^-$	0.96	0.128	0.033
$\oplus\cdot FCH_3F^-$	0.96	0.136	0.033

[a] *a* and *b* are defined in the text.

We have shown in the energetic study that placement of a counterion close to the fluorine atom bonded to the methyl group causes a spontaneous methyl transfer. We shall now analyze how the placement of this counterion changes the charge density at a and b, that is, the critical points of the bonds that are broken and formed during the chemical reaction.

In Table II we present the values of the charge densities at a and b for the unperturbed system, and the perturbed system because of the placement of a Li^+ cation at 1.66 Å, and the placement of H^+ or positive charge at 1.07 and 0.96 Å. The presence of a counterion always causes a change in charge density that translates into a large weakening of the $F–CH_3$ bond and a slight strengthening of the $CH_3–F^-$ bond. In the case when the counterion is placed at 1.07 Å, Table II shows that the positive charge diminishes the charge density at the breaking bond critical point to 0.141, down from 0.182 for the unperturbed system. An analogous diminution in charge density can be obtained if the unperturbed $F–CH_3$ bond is stretched by 0.14 Å. This fact shows again that the external perturbation due to this presence of the counterion belongs to the reaction coordinate, since this presence is equivalent to a distortion of 0.14 Å in the $F–CH_3$ bond, which clearly belongs to the internal components of the reaction coordinate.

A second analysis can be made from the Table II. One can see that both at 1.07 and 0.96 Å the change in charge density at the $F–CH_3$ bond critical point caused by the presence of a H^+ cation is larger than the change due to the presence of a positive charge. The reason is that, whereas a positive charge generates only a polarization of the electronic cloud of the FCH_3F^- system, a H^+ cation produces a charge-transfer effect as well. At 0.96 Å, the charge-transfer effect accounts for 14% of the total change in charge density at the $F–CH_3$ bond critical point, whereas at 1.07 Å it accounts for 18%. This means that the electronic cloud polarization effect decreases in a much faster way than the charge-transfer effect with the lengthening of the counterion–fluorine distance. Therefore, use of only one positive charge as a counterion is a very simplified model, because it does not take into account the charge-transfer effect.

Conclusions

The reaction coordinate is usually defined in terms of internal parameters. In this work, we have shown that in these two charge-transfer reactions the external parameters of the counterion also intervene in the reaction coordinate. In the $(H_3O_2)^-$ system as well as in the FCH_3F^- system, fluctuations of the counterion may produce a spontaneous transfer process. In the second reaction, we have shown that approach of a counterion to the fluorine atom changes dramatically the shape of the energetic profile of the transfer process. This fact demonstrates that counterion parameters are essential in the description of the potential energy hypersurface of the charge-transfer reaction. A deeper insight on the influence of neighboring ions on these reactions has been carried out by examining the changes in charge density topology due to the presence or fluctuations of counterions. This external perturbation modifies the charge density toward the product of the reaction, in the same way that a charge density variation would be obtained by changing the internal reaction coordinate of the isolated system.

A discussion of the limitations and model employed must be carried out before a comparison of our theoretical results with experimental facts is made. First of all, solvent has not been taken into account at all, so that we have used the term "neighboring ions" instead of "ionic atmosphere" throughout the paper, since the latter requires necessarily the presence of solvent. The solvent would be expected to weaken the ionic influence; hence the size of the effects might be over-emphasized. Two reasons can account for this weakening. First, solvent causes a screening between the chemical system and the counterions, which, within a continuum model for the solvent, translates into a dielectric constant larger than 1. Second, solvent participates in the reaction coordinate as well. In particular, we have shown previously,[14-16] for the reactions studied in this paper, that solvent parameters intervene in the reaction coordinate. Therefore, immobility of solvent molecules compensates for the influence of counterion fluctuations on the energetic profile. This fact was shown, with a very simplified model, by Černusák,[20c] who found that hydration partially compensates for the effect of an external cation on proton-transfer potential curves. Another limitation of our model is that a very limited number of neighboring ions have been used. Finally, it is obvious that the quantitative results obtained are dependent on the level of calculation employed. In spite of these three limitations, we think that the results obtained in the present work can be extended qualitatively to processes in solution, so that they can be applied to the ionic atmosphere. As a matter of fact, it seems that neighboring ion motions must be invoked to explain experimental results in several redox processes obtained for concentrated solutions of electrolytes.[41]

From the foregoing considerations, ionic atmosphere movements and motions of the chemical system have been shown to be correlated. This correlation does not mean that the two motions need to be simultaneous. If the two motions are not coupled, one can think of three possibilities. One possibility consists of carrying out the chemical reaction first, followed by a relaxation of the ionic atmosphere. Another possibility consists of a fluctuation of the ionic atmosphere first, followed by the chemical reaction. For a charge-transfer reaction, this means that the charge transfer adjusts itself to the fluctuations of the ionic atmosphere. A third possibility consists of an initial partial fluctuation of the ionic atmosphere, followed by the chemical process, and a final relaxation of the ionic atmosphere that leads to the products. This third mechanism is thought to occur for the solvent[42,43] and for the ionic atmosphere[19] in outer-sphere electron-transfer processes. Besides these points of view, where no coupling between both motions appears, another point of view consists of the simultaneity of the two kinds of motions. In the traditional static contribution of the ionic atmosphere, the latter will always be in equilibrium with the reacting chemical system, so it will just affect the height of the potential energy barrier. Thus, from this point of view, the ionic atmosphere will be adjusted to the chemical system by means of a relaxation. However, in this paper we have shown that the role of the ionic atmosphere is much more active. Not only the height of the barrier will be affected, but also the structure of the transition state will be changed. Since ionic atmosphere parameters do belong to the reaction coordinate, one cannot say that there is an equilibrium between the ionic atmosphere and the chemical system. Thus, fluctuations of the ionic atmosphere may induce the chemical reaction.

To discuss whether neighboring ions movements and the charge-transfer process are coupled or uncoupled, it would be necessary to take the time into account with molecular dynamics calculations. Although this dynamic study on the coupling between movements is still missing, we think that we have demonstrated that neighboring ions parameters, since they belong to the reaction coordinate, have a much more active role in the chemical process that previously thought.

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Registry No. FMe, 593-53-3; F^-, 16984-48-8; H_2O, 7732-18-5; OH^-, 14280-30-9.

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[41] Sánchez-Burgos, F.; Bertrán, J.; Carmona-Guzmán, M. C. *Rev. Inorg. Chem.* **1985**, *6*, 259.

[42] Marcus, R. A. *J. Chem. Phys.* **1956**, *24*, 966.

[43] Levich, V. G. In *Physical Chemistry*; Eyring, H., Henderson, O., Jost, W., Eds.; Academic Press: New York, 1970; Vol. 9B, p 985.

Broken Symmetry Analysis of Spin Coupling in Iron-Sulfur Clusters

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Abstract: We present a method to estimate antiferromagnetic coupling constants for polynuclear transition-metal complexes containing three or more metal sites, starting from broken symmetry molecular orbital calculations. The specific case of three $S = 5/2$ spins that occurs in linear and "cubane" 3Fe-4S clusters is illustrated through scattered wave calculations on $[Fe_3S_4(SH)_4]^{3-}$ and $[Fe_3S_4(SH)_3]^{2-}$. The trends in coupling constants agree with experimental data, but computed values are generally significantly larger than those observed. Prospects for other calculations that use this method are discussed.

The ground states of many polynuclear transition-metal complexes exhibit "antiferromagnetic" coupling, in which the spin vectors associated with the individual metal ions are aligned in opposing directions. Some of the simplest examples of this behavior are found in synthetic and naturally occurring iron-sulfur clusters, in which high-spin Fe(II) or Fe(III) ions are bridged by sulfides.[1] A variety of such structures are known, including those

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