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Ab Initio Study of the Diels−Alder Reaction of Cyclopentadiene with Acrolein in a Ionic Liquid by KS-DFT/3D-RISM-KH Theory

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Abstract: We study the Diels−Alder reaction between cyclopentadiene and acrolein in a model room-temperature ionic liquid ([mmim][PF$_6$]) as a solvent. The calculations have been performed with the KS-DFT/3D-RISM-SCF theory, where the reactants and transition state (TS) have been represented at a QM level, while the solvent is represented by a 3D distribution of classical (charge + LJ) sites obtained by solving the 3D-RISM integral equation. We show that this method, being computationally efficient, is able to reproduce the main experimental features displayed by the experiments, concerning the reaction rate enhancement and augmentation of the endo/exo ratio in ionic liquids (ILs). We find that the IL distorts noticeably the transition state geometry, inverting the order of the frontier orbitals and leading to an enhancement of the asynchronicity of the reaction. Finally, we find, in agreement with recent work, that formation of the hydrogen bond between the unique C2 hydrogen of the imidazolium ring is not essential to explain the peculiar features of these reactions in ILs.

Introduction

Ionic liquids (ILs) are salts generally constituted by a bulky organic cation and a polyatomic anion, liquid at or near room temperature, whose popularity has expanded dramatically in the last 10 years due to their recognition as new green chemicals with unique and highly tunable physicochemical properties.[1] They are now being explored in virtually all areas of chemistry as process chemicals (solvents, separation media, etc.), performance chemicals (lubricants, electrolytes, etc.), and materials. Studies of organic reactions and catalyzed processes performed in ILs suggest that for many reactions ILs give improved results in terms of yields, selectivity, and rate. Constituted exclusively by ions, ILs represent a reaction environment completely different from molecular solvents.[2] The strong ion−ion interactions present in ILs lead to highly structured materials, three-dimensional supermolecular polymeric networks of anions and cations linked by H bonds and/or Coulombic interactions, often permeated by nonpolar regions due to the presence of sufficiently long alkyl chains on cation.[3] Like many other organized systems, the ILs environment can display not only dynamic but also local heterogeneity; molecules are trapped for a relatively long period in a quasistatic local solvent cage.[4] However, despite this complexity, reactivity and selectivity in ILs are generally explained considering the ability of the constituting cations and anions to act as hydrogen-bond donors/acceptors and the degree of charge delocalization in the anion.[5,6] In other words, they are normally rationalized on the basis of microscopic properties of these media, neglecting the solvent effects that can arise from the bulk and its supermolecular organization.

Generally, solvent effects on chemical reactions may be considered at the theoretical level; however, whereas for molecular solvents a continuum method[7] can be used with good results, the nature of ILs requires the definition of a more appropriate computational model. Recently, we have shown the possibility to adopt the KS-DFT/3D-RISM-KH method to study the solvation ability of ILs.[8] The method predicts the IL properties in remarkable agreement with conclusions drawn from MD simulations: the three-dimensional solvation structure is reproduced well, and the solvent environment effect of the constituents of the IL is described correctly.

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The study described herein aims to apply this approach to the treatment of organic reactions in ILs. In particular, we report here data on the Diels−Alder reaction of cyclopentadiene with acrolein in dimethylimidazolium hexafluorophosphate, [mmim][PF$_6$].

Diels−Alder reaction has been widely investigated also in ILs.[9] Recently, in collaboration with the group of Welton, we evidenced[10] that the stereochemical and kinetic behavior of reaction of cyclopentadiene with three different dienophiles (including acrolein) in ILs is a function of *both* the solvent and the solute. Using multiparameter linear solvation energy relationships, the primary role of the solvent hydrogen-bond donation ability (α) has been evidenced in the reactions of acrolein and methyl acrylate but not of acrylonitrile. An attempt to study the same reaction at the DFT level using a supermolecular approach, i.e., considering a three molecule system constituted by diene, dienophile, and IL cation, has shown[11] that the IL cation coordination affects the equilibrium geometries and electronic structures of the reacting species throughout the reaction pathway, leading to changes in reactivity and selectivity. On the other hand, this approach did not allow the evaluation of more concerted interactions. The "clamp" effect, arising from the ability of the cation to interact with the dienophile and from the fact that in the IL the freedom of motion of the cation is strongly limited by the Coulombic interactions with the solvent bulk, could be only hypothesized using this approach.[11]

In the present work, we focused on understanding the role of the electronic and solvation energies on the catalytic and selectivity effects displayed by ionic liquids in Diels−Alder reactions by a multicomponent QM/classical method relying on 3D-RISM/SCF theory developed[12] in recent years and recently applied by some of us to ionic liquids.[8]

It is however noteworthy that during the writing of this paper a communication on the Diels−Alder reaction of cyclopentadiene with methyl acrylate in dimethylimidazolium chloride, [mmim]Cl, using the multicomponent reference interaction site model (RISM) has been published.[13] Therefore, results obtained adopting KS-DFT/3D-RISM-KH will be discussed in light of the experimental results taking into account the recently published data.

Computational Method

In this study, we chose 1,3-dimethylimidazolium hexafluorophosphide ([mmim][PF6]), which we consider a reasonable approximation to 1-butyl-3-methylimidazolium hexafluorophosphide ([bmim][PF6]), one of the most popular ILs on which experimental results for Diels−Alder reactions are available.[10]

The KS-DFT/3D-RISM-SCF procedure has been described in detail in previous work; here, we summarize only the main outline of the procedure.

The presence of the solvent is accounted for by a 3D distribution of solvent sites (described as rigid molecules) around the solute molecule, which is obtained[12] by the standard 3D-RISM integral equation ([3D-RISM]); the solute is described by its electron density distribution in space plus the nuclei charge (which describe the Coulomb interaction), while the dispersion interaction is described by Lennard−

Table 1. Free Energy of the Reagents (in kcal/mol) in the Gas Phase (gas) and in the Ionic Liquids Solution (IL) Together with Electronic (ΔE_{el}), Solvation (μ), and Thermal Correction (kinetic contribution + zero-point energy)

	ΔE_{el}	ΔG_{therm}	$\Delta \mu$	ΔG_{total}
cis-acrolein (gas)	−1618.40	12.45		−1605.95
trans-acrolein (gas)	−1627.95	13.08		−1614.87
cyclopentadiene (gas)	−2207.97	32.00		−2175.97
cis-acrolein (IL)	−1626.91	13.36	22.63	−1590.92
trans-acrolein (IL)	−1627.38	13.14	24.38	−1589.86
cyclopentadiene (IL)	−2207.33	31.82	25.51	−2150.00

Jones sites centered on each nucleus. The electronic structure of the solute (reagents, TS, products) and the 3D solvent structure are then obtained self-consistently.

The KS-DFT/3D-RISM-SCF were performed on a grid of 32 × 32 × 32 points spaced by 0.5 Å. The RISM equations were solved together with the partially linearized hypernetted chain (PLHNC) closure, which has been shown to give the most reliable results for ionic liquids.[14]

The geometries of the reactants, transition states, and products were optimized both in the gas phase and in the solvent at the DFT level with the TZ2P basis set and the OLYP XC functional. The vibrational frequencies were calculated on each final geometry at the same level. Since in the Diels−Alder reaction the π−π interaction plays a crucial role, the final electronic energy changes on optimized structures were calculated with the M06−2X functional, which is to date most accurate in predicting the π−π dispersion interaction.[15]

The frequency calculations in the IL solvent gave some spurious imaginary frequencies at very low wavenumbers in addition to the imaginary frequency relative to the reaction coordinate; this effect has been ascribed to the presence of the solvent, whose 3D distribution remains frozen during the frequency run. To evaluate the thermal contribution, the frequencies were then recalculated on the TS geometries fully optimized in IL but in a subsequent run without the solvent.

The correct finding of transition states and of the reaction coordinate was confirmed by performing an IRC run on each TS[16] in order to verify that the actual products (in the forward direction) and reagents (in the backward direction) were obtained.

All computations were performed with a development version of the ADF code.[17]
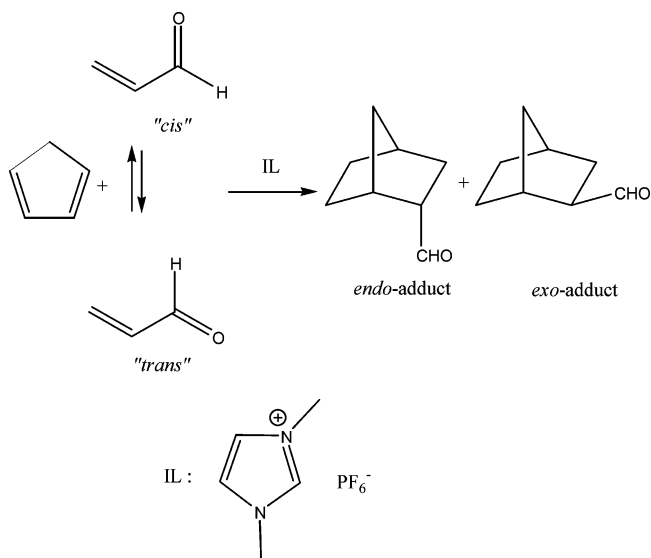
Results and Discussion

We start our analysis by examining the different reactions that can take place in both the gas phase and IL solution. In Table 1 the relative activation free energies $\Delta G^{\ddagger}$ are reported for transition state (TS) barriers.

The first thing that we note is that the reaction pathways to be considered change when switching from the gas phase to the IL solvent. The dienophile can be found in two different conformations, which are usually referred to as "cis" or "trans" according to the position that the double bonds can take with respect to the single C−C bond. Furthermore, dienophile can interact with cyclopentadiene following the endo or exo approach to give the corresponding adducts;

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Table 2. Activation Free Energy $\Delta G^{\ddagger}$ (in kcal/mol) in the Gas Phase (gas) and in the Ionic Liquids solution (IL) Together with Electronic (ΔE_{el}), Solvation (μ), and Thermal Correction (kinetic contribution + zero-point energy) Contributions, and Numerical Value of the Imaginary Frequency of the Normal Mode Corresponding to the Reaction Coordinate

	ΔE_{el}	$\Delta\mu$	ΔG_{therm}	$\omega(cm^{-1})$	$\Delta G^{\ddagger}$
X–T(gas)	12.86		19.29	378.20	32.15
N–T(gas)	12.29		19.05	376.40	31.84
X–T(IL)	16.73	−10.05	19.82	359.78	26.50
N–T(IL)	15.88	−10.15	19.70	358.98	25.43
X–C(IL)	12.38	−6.47	19.48	338.57	25.39
N–C(IL)	10.74	−6.69	19.31	339.22	23.36

therefore, four possible structures for the TSs (endocis(N–C), endotrans(N–T), exocis(X–C), and exotrans(X–T)) must be considered.
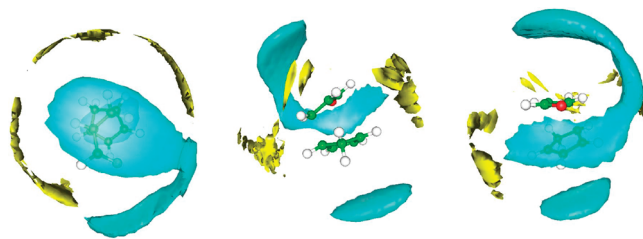

Figure 1. 3D distribution function of the anion (yellow) and cation (N site, light blue) around the transition state optimized in the IL solvent.
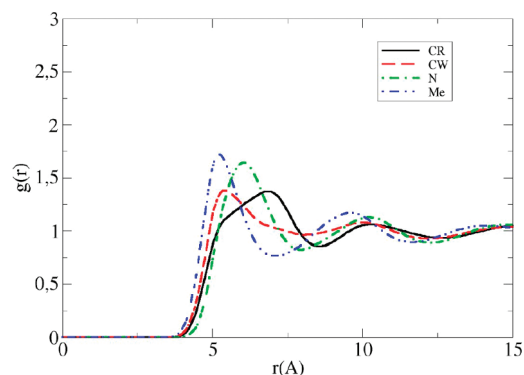

Figure 2. Radial distribution function of cation sites with respect to the distance *r* from the transition state geometric center.
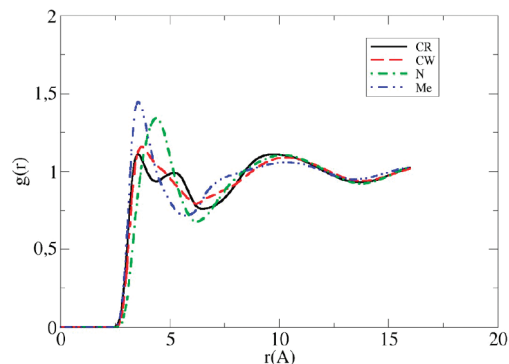

Figure 3. Radial distribution function of cation sites as a function of distance *r* with respect to the carbonyl oxygen of the TS.

In the void, the dienophile can be found only as a trans conformer due to the large energy difference ($\Delta G = 8.92$ kcal/mol, see Table 1) between the two isomers; thus, the reaction in the gas phase can take place only through the exotrans and endotrans TSs. This is the first difference with the work by Sato and co-workers,[13] where only the cis structure was considered due to their lower TS energies. In solution (see Table 1) both conformers are present, with a cis:trans ratio of about 75:25; in addition, the reaction free energy barrier height is lower (about 2 kcal/mol, see Table 2) for the endocis TS with respect to both TSs with the trans isomer. Thus, the cis route is actually the more important pathway to products, but the presence of the trans isomer in solution is not negligible.

The presence of the ionic liquid solvent implies changes at an electronic and a structural level on the transition state; on the other side, the thermal contribution to free energy was found to change negligibly (at most by 0.2 kcal/mol) when passing from the optimized structure in the gas phase to the optimized structure in the IL. To such effects, the solvation free energy contribution $\Delta\mu$ must be added to understand the effect of the solvent on the reaction.

Interaction with the Solvent. The interaction of the transition state with the solvent can be analyzed on the basis of the 3D distribution functions of the anion and cation around the transition state, presented in Figures 1–3. The cation density around the transition states has its peaks mainly at the carbonyl oxygen and in two regions above and below the TS, parallel to the diene and the dienophile planes. Thus, the interaction is driven by oxygen–hydrogen coupling, but also stacking interactions between the TS and the cation can be detected. The anion is located on the imaginary plane which is about perpendicular to the reaction coordinate, less close than the cation to the TS. It appears then that the first solvation shell of the TS could be described by three cations (one coordinated with the carbonyl and two stacked above and below the TS) and three anions.

This can be confirmed by inspection of the 1D averaged pair distribution functions (Figure 2), where the TS-cation has two peaks at short distance: the first is given by the cation directly interacting with the carbonyl while the second by

the stacked ones. It is noteworthy that the interaction of the carbonyl oxygen is stronger with the methyl groups and the twin CW sites than with the single CR group; thus, in agreement with precedent findings by Jorgensen,[18] this suggests that the hydrogen bond with the single hydrogen posed on CR is not a key factor and that interactions with other hydrogen sites are more important in driving the reaction.

Structural Level. The ionic liquid changes the geometry of the TS for all four pathways considered, deforming the diene−dienophile stacking geometry and enhancing the asynchronicity of the reaction when performed in these solvents. This aspect has been evidenced in previous theoretical studies[19] in which a single cation was allowed to interact with the TS, forming a hydrogen bond with the carbonyl oxygen; this aspect was not considered in the work of Sato,[13] where the geometries considered were those obtained in the gas phase. Also, the subsequent reduction of the imaginary frequency for the solvated TS when compared to the gas phase one, found in previous studies,[14] has been reproduced by us without the need for a specific quantum-mechanical interaction between the IL cation and the substrate. Then, even if it appears consolidated that the asynchronicity of the reaction is enhanced in ILs, it appears from our calculations that this aspect is not necessarily related to the presence of strong hydrogen bonding between the unique ring hydrogen and the dienophile (this aspect was first suggested by Acevedo and Jorgensen[18]).

Electronic Level. The presence of the ionic liquid raises the electronic energy of the TS by about 2−5 kcal/mol; this rise is accompanied by a switching of the order of the two frontier orbitals HOMO and HOMO−1. The combined effect of geometry distortion and electronic modification of the TSs leads to a large modification of the dipole moment of the TS, passing from 4.11 to 6.09 D for the exocis form and from 4.24 to 5.97 D for the endotrans form. The energy of these levels is slightly lower in the endo-TS with respect to the exo-TS; nevertheless, the electronic energy of the endocis transition state is lower than the exocis by 1.64 kcal/mol (see Table 2). This will play a key role in selectivity, as will be shown in the following discussion.

Solvation Free Energy. The most important effect on the reaction rate is given by the solvation free energy. The difference in $\Delta\mu$ between the isolated reagents and the transition state amounts to 8−10 kcal/mol, giving a substantial contribution to the barrier lowering in ILs, very similar to what happens in water.[20] This conclusion, already evidenced in the very recent paper by Sato and co-workers,[13] can be further investigated by inspecting the contribution of electronic and solvation contributions to free energy, which are reported in Figure 4; here, it can be appreciated that there is a minimum in solvation energy in correspondence of the TS geometry. The presence of a generalized solvophobic effect on neutral solutes in ILs with features very similar to that of water has been recently pointed out;[21] at present, it is believed that the (generally positive) solvation free energy of a neutral solute in a ionic liquid is dominated by the unfavorable process of creating a cavity of suitable size to accommodate the solute, which for an ionic liquid requires
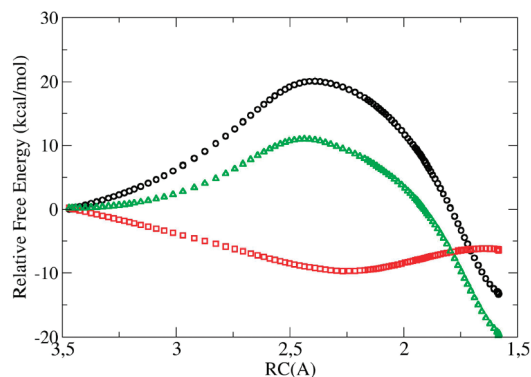

Figure 4. Contribution of electronic energy (black circles) and solvation energy (red squares) to reaction free energy (green triangles) as a function of reaction coordinate. The thermal and zero-point correction to free energy are not reported here.

a considerable amount of work due to the lowering of the Coulombic interactions, which cannot be recovered by dipole−ion (or even less efficient) interaction.[22]

For this reason, the aggregation of the organic moieties in ILs is strongly favorable, and this aspect drives the reaction rate in ionic liquids. A more detailed discussion of this aspect will be presented in the following discussion.

Endo/Exo Ratio. The endo/exo ratio has been studied and found, on the basis of M06-2X results, to be consistent with experiments and previous calculations; the difference in energy between the endocis-TS and the exocis-TS is found to be 2.03 kcal/mol, while the one between endotrans and the exotrans is 1.07 kcal/mol. Taking into account the relative equilibrium amount of *cis*- and *trans*-acrolein, an endo/exo ratio of 88:12 was found, while the corresponding ratio in the void was found to be about 70:30. The ionic liquid thus enhances the endo selectivity of the reaction, in agreement with experiments.[10] By inspection of Table 2, it can be readily seen that the origin of this enhancement is due to the electronic contribution to the free energy, which is lower in the endocis structure; conversely, the excess solvation free energy, which enhances the importance of the trans reaction route, appears to play a negligible role on the selectivity rise. This appears to go in the opposite direction with respect to water, in which the endo selectivity enhancement was found to be due to excess free energy of solvation, as already shown;[13] nevertheless, the electronic origin of the enhanced selectivity was not investigated in detail.

This favorable electronic reorganization energy in the endo TS conformer has been suggested by some of us to be due to the relative orientation of the π system of the diene with respect to the activated dienophile.[11] To confirm this, the obtained structures have been analyzed by taking into account the energies obtained at the OLYP level, which is not as good as M06-2X, to take into account the $\pi-\pi$ interaction.[15] At the OLYP level, the obtained endo/exo ratio was 1.40 in the IL, while in the void the exo product was slightly more probable than the endo product.

The ionic liquid can be probably thought to enhance the $\pi-\pi$ dispersion interaction between the reactants: from comparison of the two different functionals, it is nevertheless

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evident that a proper description of $\pi-\pi$ interaction is mandatory to obtain reliable results about the endo selectivity.

Conclusions

In this work, we applied KS-DFT/3D-RISM-SCF to the Diels−Alder reaction in room-temperature ionic liquids. This method is able to obtain results in general agreement with experiment and proposes itself as a very powerful analysis method for processes in ionic liquids. Our results are in general agreement with results displayed by Sato and co-workers, which for the first time applied a mixed QM/RISM approach to this reaction in a ionic liquid. We go further on the direction pointed by this last work by analyzing the effect of the IL on the electronic and geometric structure of adducts.

The structure of the TS is deformed by the presence of the IL, and the asynchronicity of the reaction is augmented; the frequency of the barrier passing is nevertheless slightly lowered in ILs.

The importance of the hydrogen bonding between unique CR and carbonyl oxygen has been revised and found to be not of capital importance for the reaction. Both aspects were already noticed by Jorgensen with much more sophisticated calculations.

The rate acceleration observed in ILs is given by the free energy of solvation, which promotes aggregation of nonionic molecules in ILs solutions. On the other side, the endo selectivity enhancement in ILs is driven by electronic energy, which comes probably from the most favorable $\pi-\pi$ interaction between the reactants, which is enhanced in IL.

References

(1) Ionic Liquids IIIB: Fundamentals, Progress, Challenges, and Opportunities-Transformations and Processes. *ACS Symposium Series 902*; Rogers, R. D., Seddon, K. R., Eds.; American Chemical Society: Washington, D.C., 2005. Ionic Liquids IIIA: Fundamentals, Progress, Challenges, and Opportunities-Properties and Structure. *ACS Symposium Series 901*; Rogers, R. D., Seddon, K. R., Eds.; American Chemical Society: Washington, D.C., 2005. In *Ionic Liquids in Synthesis*, 2nd ed.; Wasserscheid, P., Welton, T., Eds.; Wiley-VCH: Weinheim, 2007.

(2) Chiappe, C.; Pieraccini, D. *J. Phys. Org. Chem.* **2005**, *18*, 275.

(3) (a) Lopes, J. N. A.; Padua, A. A. H. *J. Phys. Chem B* **2006**, *110*, 3330. (b) Chiappe, C. *Monatsh. Chem.* **2007**, *137*, 1035. (c) Xiao, D.; Rajian, J. R.; Hines, L. G.; Li, S.; Bartsch, R. A.; Quitevis, E. L. *J. Phys. Chem B* **2008**, *112*, 13316. (d) Consorti, C, S.; Suarez, P. A. Z.; de Souza, R. F.; Burrow, R. A.; Farrar, D. H.; Lough, A. J.; Loh, W.; da Silva, L. H. M.; Dupont, J. *J. Phys. Chem. B* **2005**, *109*, 4341.

(4) Hu, Z.; Margulis, C. J. *Proc. Natl. Acad. Sci. U.S.A.* **2006**, *103*, 831.

(5) (a) Lancaster, N. L.; Welton, T. *J. Org. Chem.* **2004**, *69*, 5986. (b) Anderson, J. L.; Ding, J.; Welton, T.; Armstrong, D. W. *J. Am. Chem. Soc.* **2002**, *124*, 14247. (c) Crowhurst, L.; Lancaster, N. L.; Perez Arlandis, J. M.; Welton, T. *J. Am. Chem. Soc.* **2004**, *126*, 11549. (d) Lancaster, N. L.; Salter, P. A.; Welton, T.; Young, G. B. *J. Org. Chem.* **2002**, *67*, 8855. (e) Chiappe, C.; Pieraccini, D. *J. Org. Chem.* **2004**, *69*, 6059. (f) Grodkowski, J.; Neta, P.; Wishart, J. F. *J. Phys. Chem. A* **2003**, *107*, 9794. (g) Skrzypczak, A.; Neta, P. *J. Phys. Chem. A* **2003**, *107*, 7800. (h) D'Anna, F.; Frenna, V.; Noto, R.; Pace, V.; Spinelli, D. *J. Org. Chem.* **2006**, *71*, 5144. (i) Chiappe, C.; Pieraccini, D.; Sullo, P. *J. Org. Chem.* **2003**, *68*, 6710. (l) Bini, R.; Chiappe, C.; Pieraccini, D.; Piccioli, P.; Pomelli, C. S. *Tetrahedron Lett.* **2005**, *46*, 6675. (m) Crowhurst, L.; Falcone, R.; Lancaster, N. L.; Llopsis-Mestre, V.; Welton, T. *J. Org. Chem.* **2006**, *71*, 8847. (n) Hallet, J. P.; Liotta, C. L.; Ranieri, G.; Welton, T. *J. Org. Chem.* **2009**, *74*, 1864.

(6) Harper, J. B.; Kobrak, M. N. *Mini-Rev. Org. Chem.* **2006**, *3*, 253.

(7) Tomasi, J.; Mennucci, B.; Cammi, R. *Chem. Rev.* **2005**, *105*, 2999.

(8) Malvaldi, M.; Bruzzone, S.; Chiappe, C.; Gusarov, S.; Kovalenko, A. *J. Phys. Chem. B,* **2009**, *113*, 3536.

(9) (a) Lee, C. W. *Tetrahedron Lett.* **1999**, *40*, 2461. (b) Agarwal, A.; Lancaster, N. L.; Sethi, A. R.; Welton, T. *Green Chem.* **2002**, *4*, 517. (c) Earle, M. J.; McCormac, P. B.; Seddon, K. R. *Green Chem.* **1999**, *1*, 23. (d) Fischer, T.; Sethi, A. R.; Welton, T.; Woolf, J. *Tetrahedron Lett.* **1999**, *40*, 793. Howarth, J.; Hanlon, K.; Fayne, D.; McCormac, P. *Tetrahedron Lett.* **1997**, *38*, 3097. (e) Vidis, A.; Ohlin, C. A.; Laurenczy, G.; Küster, E.; Sedelmeier, G.; Dyson, P. J. *Adv. Synth. Catal.* **2005**, *347*, 266. Silvero, G.; Arévalo, A. J.; Bravo, J. L.; Jiménez, J. L.; López, I. *Tetrahedron* **2005**, *61*, 7105. (f) Sarma, D.; Kumar, A. *Appl. Catal., A* **2008**, *335*, 1.

(10) Bini, R.; Chiappe, C.; Llopsis Mestre, V.; Pomelli, C. S.; Welton, T. *Org. Biomol. Chem.* **2008**, *6*, 2522.

(11) Bini, R.; Chiappe, C.; Llopsis Mestre, V.; Pomelli, C. S.; Welton, T. *Theor. Chem. Acc.* **2009**, *123*, 347.

(12) Kovalenko, A.; Hirata, F. *Chem. Phys. Lett.* **1998**, *290*, 237. Kovalenko, A.; Hirata, F. *J. Chem. Phys.,* **1999**, *110*, 10095.

(13) Hayaki, S.; Kido, K.; Yokogawa, D.; Sato, H.; Sakaki, S. *J. Phys. Chem. B* **2009**, *113*, 8230.

(14) Malvaldi, M.; Bruzzone, S.; Chiappe, C. *Phys. Chem. Chem. Phys.* **2007**, *9*, 5576.

(15) Zhao, Y.; Truhlar, D. G. *Acc. Chem. Res.* **2008**, *41*, 157.

(16) Deng, L.; Ziegler, T. *Int. J. Quantum Chem.* **1994**, *52*, 731.

(17) ADF2008.01, SCM, Theoretical Chemistry, Vrije Universiteit, Amsterdam, The Netherlands, http://www.scm.com (accessed June 8, 2009).

(18) Acevedo, O.; Jorgensen, W. L.; Evanseck, J. D. *J. Chem. Theory Comput.* **2007**, *3*, 132.

(19) Sun, H.; Zhang, D.; Ma, C.; Liu, C. *Int. J. Quantum Chem.* **2007**, *107*, 875.

(20) Harano, Y.; Sato, H.; Hirata, F. *J. Am. Chem. Soc.* **2000**, *122*, 2289.

(21) Koddermann, T.; Pascheck, D.; Ludwig, R. *Phys. Rev. Lett.* **2008**, *100*, 115901.

(22) Kobrak, M. N. *J. Phys. Chem. B* **2007**, *111*, 4755. Pomelli, C.; Malvaldi, M.; Chiappe, C. *Pure Appl. Chem.* **2009**, *81*, 767.