Summary of recent publications

Theoretical Study of the Gas-Phase Reaction of Fluoride and Chloride Ions with Methyl Formate

J. R. Pliego Jr., J. M. Riveros,

Abstract. The potential energy surface of the gas-phase reaction between halide ions (F^- and Cl^-) and methyl formate has been investigated by ab initio calculations. For F^-, two pathways have been observed at thermal energies and identified in the calculations: 1) α-elimination of CO to yield a fluoride–methanol adduct, the so-called Riveros reaction that has found wide application in gas-phase ion chemistry, and 2) S_N2 displacement of $HCOO^-$. The first reaction is shown to proceed by the initial formation of a loose complex followed by formal abstraction of a formyl hydrogen to yield a three-body complex that dissociates into the final products. The S_N2 reaction initially involves formation of a loose complex with the fluoride attached to the methyl group of the ester. The first pathway is calculated to go through a lower energy local transition state than the corresponding S_N2 reaction but the transition states are located below the energy of the reagents. Both ion-neutral complexes can interconvert via formation of a stable tetrahedral intermediate. The product distribution was estimated via a simple RRKM calculation that predicts 92% of α-elimination and 8% of S_N2 reaction. This prediction is in excellent agreement with measurements carried out by FT-ICR. This product distribution is predicted to remain essentially unchanged for the reaction with $DCOOCH_3$ in agreement with experimental observations. A similar analysis of the corresponding Cl^- + $HCOOCH_3$ reaction reveals that α-elimination has a substantial activation energy (well above the reagents) accounting for the failure to observe this reaction even though it is exothermic. These calculations also reveal that for the Cl^- system, the tetrahedral intermediate is not a stable intermediate in agreement with previous experimental data on related systems.

The cluster-continuum model for the calculation of the solvation free energy of ionic species

J. R. Pliego Jr., J. M. Riveros,

Abstract. A hybrid approach using a combination of explicit solvent molecules and the continuum IPCM method is proposed for the calculation of the solvation thermodynamic properties of ions. This model, denominated cluster-continuum, has been applied to the calculation of the solvation free energy of 14 univalent ions, mainly organic species, and compared with the results obtained with the IPCM, PCM and SM5.42R continuum methods. The average error in our calculated solvation free energies with respect to experimental data is 8.7 kcal mol^{-1}. However, the great merit of our model resides in the homogeneous treatment for different ions, resulting in a standard deviation of only 2.9 kcal mol^{-1} for the average error. Our results suggest that the cluster-continuum model must be superior to the IPCM, PCM and SM5.42R methods for studying chemical reactions in the liquid phase, since these continuum methods present a standard deviation of ~ 8 kcal mol^{-1} for the average error for the species studied in this work. The model can

also be used to calculate the solvation entropy of ions. Predicted solvation entropies for five ionic species are in good agreement with available experimental data.

On the electron affinity of $X_nGe(OMe)_{3-n}$ radicals (X = H, F; n = 0 - 2) and the Ge-H bond dissociation energy

N. H. Morgon, J. M. Riveros,
Int. J. Mass Spectrom. **2001**, *210-211,* 173-180.

Abstract. The recent observation of a number of gas-phase germyl anions of the type $X_nGe(OMe)_{3-n}^-$ (X = H, F; n = 0 − 2), suggests that these species are very stable and relatively unreactive in ion/molecule reactions. In this paper, we report the electron affinity of the corresponding radicals calculated at the QCISD(T) level using basis sets developed by the generator coordinate method and adapted to effective core potentials. These calculations show the electron affinity increasing in the order GeH_3 (1.55 eV) < H_2GeOMe (1.75 eV) < $HGe(OMe)_2$ (1.95 eV) < $Ge(OMe)_3$ (2.32 eV) < $FGe(OMe)_2$ (2.67 eV) < F_2GeOMe (3.12 eV), and are estimated to be within 0.10 eV to 0.15 eV (for the radicals at the upper end) of the true adiabatic values. Ge-H bond energies have also been calculated for some of the simpler systems and the 81.1 kcal mol^{-1} BDE_{0K} calculated for H_3Ge-H is in very good agreement with the recommended experimental value of 82 ± 2 kcal mol^{-1}.

Potential energy surface for the photoelectron spectrum of $[CH_3OHBr]^-$

N. H. Morgon, J. M. Riveros,
J. Mol. Struct. (THEOCHEM) **2001**, *539*, 135-143.

Abstract. A high level theoretical methodology that makes use of pseudopotentials coupled with the generator coordinate method to develop an appropriate valence basis set has been applied to the characterization of the ion and neutral surface relevant to the photoelectron spectrum of the $[CH_3OHBr]^-$ ion. The threshold wavelength for vertical photodetachment is predicted at 310.6 nm and the adiabatic threshold wavelength at 312.5 nm, in excellent agreement with the reported onset at 309 ± 1.3 nm [J. Phys. Chem. A, 101 (1997) 2371]. The calculated binding energy for $(CH_3OH)Br^-$ is predicted to be 57.6 kJ.mol^{-1}, in close agreement with the most recent experimental determination by high pressure mass spectrometry of 60.7 kJ mol^{-1}. Furthermore, our calculations show that if the experimental threshold photodetachment corresponds to the vertical process, excellent agreement is observed between the dissociation energy of $(CH_3OH)Br^-$ derived from the spectroscopic and mass spectrometric experiments.

The Gas Phase Reaction between Hydroxide Ion and Methyl Formate: A Theoretical Analysis of the Energy Surface and Product Distribution

J. R. Pliego Jr., J. M. Riveros,
Chem. Eur. J. **2001**, *7*, 169-175.

Abstract. The potential energy surface for the prototype solvent-free ester hydrolysis reaction: OH^- + $HCOOCH_3 \rightarrow$ products has been characterized by high level ab initio calculations of MP4/6-311+G(2df,2p)//MP2/6-31+G(d) quality. These calculations reveal

that the approach of an OH⁻ ion leads to the formation of two distinct ion-molecule complexes: 1) the MS1 species with the hydroxide ion hydrogen bonded to the methyl group of the ester, and 2) the MS4 moiety resulting from proton abstraction of the formyl hydrogen by the hydroxide ion and formation of a three-body complex of water, methoxide ion and carbon monoxide. The first complex reacts to generate formate anion and methanol products through the well known $B_{AC}2$ and S_N2 mechanisms. RRKM calculations predict that these pathways will occur with a relative contribution of 85% and 15% at 298.15 K, in excellent agreement with experimentally measured values of 87% and 13% respectively. The second complex reacts by loss of carbon monoxide to yield the water-methoxide complex through a single minimum potential surface and is the preferred pathway in the gas-phase. This water-methoxide adduct can further dissociate if the reactants have excess energy. These results provide clear evidence that the preferred pathways for ester hydrolysis in solution are dictated by solvation of the hydroxide ion.

New Values for the Absolute Solvation Free Energy of Univalent Ions in Aqueous Solution

J. R. Pliego Jr., J. M. Riveros,
Abstract. The absolute solvation free energy of 30 univalent ions, mainly organic species, has been calculated from experimental and theoretical data on proton affinities, aqueous acidity constants, solvation free energy of neutral species, and the new value for the absolute solvation free energy of the proton determined by Tissandier et al (J. Phys. Chem. A 102 (1998) 7787). Our new values reveal considerable differences with previous compilations, and should be taken into consideration for comparison with liquid simulation results and in the development of implicit solvation models.

Experimental and Theoretical characterization of Long-Lived Triplet State $CH_3CH_2S^+$ Cations

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Abstract. Gas-phase $[C_2H_5S]^+$ ions obtained by electron impact from $CH_3SC_2H_5$ at 13 eV undergo three distinct low-pressure ion/molecule reactions with the parent neutral: proton transfer, charge transfer, and hydride abstraction. The kinetics of these reactions studied by FT-ICR techniques clearly suggests the $[C_2H_5S]^+$ species to be a mixture of isomeric ions. While proton transfer and hydride abstraction are consistent with $CH_3SCH_2^+$ and CH_3CHSH^+ reagent ions, the observed charge transfer strongly argues for the presence of thioethoxy cation, $CH_3CH_2S^+$, predicted to be stable only in the triplet state. Charge transfer reactions only occur with substrates having an IE below 8.8 eV and thus yield an upper limit for the recombination energy of the $CH_3CH_2S^+$ ions. Studies using $CD_3SC_2H_5$ show that charge transfer reactions are promoted by cations originating from a sulfur-methyl carbon bond cleavage. Ab initio calculations at several levels of theory predict that $CH_3CH_2S^+$ ions are only stable in the triplet state. Calculations along the fragmentation pathway of the molecular ion reveal the tendency to generate triplet $CH_3CH_2S^+$ ions upon cleavage of the sulfur-methyl carbon bond. Calculations were also

carried out to determine the lifetime of triplet $CH_3CH_2S^+$ using nonadiabatic RRKM theory. The exothermic or near thermoneutral spin-forbidden unimolecular isomerizations and dissociations were first characterized at different levels of theory, and the minimum energy crossing points (MECPs) for all the channels identified at the CCSD(T) level. The probability for surface hopping was then estimated from the spin-orbit matrix elements. The calculated unimolecular dissociation rate constants predict that triplet $CH_3CH_2S^+$ ions with less than 10 kcal mol^{-1} of internal energy and at any level of rotational excitation should be long lived, and strongly support the experimental observations.