Regular article

Solvent effects on molecular reactivity descriptors: some test cases

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Abstract. The reactivity of two significant classes of organometallic compounds involved in electrochemical processes, namely Co(II) N_4-macrocycles and Ru/Os polypyridyl complexes, toward the oxidation of two different electron donor molecules (2-mercaptoethanol and iodine) was investigated using first-principle theoretical methods. Two different descriptors, the donor-acceptor intermolecular hardness and the electrophilicity index, were considered for discriminating the relative reactivity of the different species toward the same electron donor. All of the calculations were carried out using a recent hybrid Hartree-Fock/Density Functional approach (PBE0) and solvent effects were included using a recent version of the polarisable continuum model (C-PCM). The influences of the metal atom, of the chemical environment, and of the medium on reactivity were analysed and compared to the available experimental data.

Keywords: Chemical reactivity indexes – Density functional theory – Solvent effects – Electrochemistry

Introduction

Electrochemistry is a wide branch of chemistry devoted to the study of electron transfer or induced electron transfer phenomena [1, 2, 3]. In principle, any electrochemical reaction involves a "flow" (directed or mediated by other chemical species) of electrons from a reducing agent to and oxidising agent; in other words, the reduction of a species and the oxidation of another. Electrochemical reactions can be used to produce energy, as in the case of photovoltaic devices [4], or to produce new species [5], or they can be involved in important biochemical processes [6]. Nevertheless, even if the basic phenomenon is rather simple, the actual experimental conditions under which it happens can be extremely tuneable and complex. For this reason, in order to understand the electrochemical process from first principles, and to eventually discover how it can be tuned, a new branch of theoretical quantum chemistry – theoretical electrochemistry – is developing [7, 8]. Its aim is to understand the electron transfer phenomenon when large molecular acceptor and donator species (such as the one studied in this paper) react in complex chemical environments (in solution and/or when adsorbed on surface) far from the idealised condition of the gas phase.

More than for other reactions, these electrochemical reactions strongly depend upon the environment since the reduced and oxidised species can be differently stabilised and so the overall reactivity can change dramatically. Therefore, any theoretical approach used to model this type of reaction in a meaningful chemical sense should be refined enough to correctly describe the change induced by a single electron transfer in a real chemical environment.

However, a full first-principles (ab initio) characterisation of real electron transfer reactions, in particular of their thermodynamics and kinetics, often remains unfeasible. One possible approach is to focus on the properties of the single molecules involved (for instance the donor and the acceptor in the electron transfer reaction), and try to define a theoretically consistent index of their electron donor and/or acceptor capability in gas phase and in solution, instead of modelling the whole process.

In this context, the global descriptors of reactivity, electronic chemical potential (μ) and chemical hardness (η) [9, 10, 11], represent a simple way of rationalizing the different chemical behaviours of similar species. In particular, μ characterizes the tendency of electrons to escape from the equilibrium system, while η can be seen as a resistance to electron transfer. These two entities are global properties of the investigated systems and the

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characterization of their profiles along a reaction coordinate has been shown to be a useful way to study their chemical reactivity [12, 13, 14, 15, 16, 17]. More recently, Parr and co-workers [18] have introduced another index, electrophilicity (ω), as a convenient parameter to assess the electrophilic power of an atom or a molecule. This electrophilicity index can be defined in term of hardness and chemical potential [18]. Although the environment (the solvent) plays an important role in most of the reactions, very few studies have been undertaken to understand its effects on the reactivity descriptors [16, 17, 19].

From a more theoretical point of view, the hardness and softness concepts receive a rigorous definition in the framework of density functional theory (DFT), allowing their non-empirical evaluation (see for instance [12, 13]). The calculation of the hardness and chemical potential requires an accurate evaluation of the system ionisation energy and electron affinity. As for other molecular properties, DFT is an invaluable tool, provided that an adequate exchange-correlation functional is used. A number of functionals based on the generalised gradient approximation (GGA) have been developed in the last few years [20, 21]. A class of them introduces fitted parameters (to a set of experimental data) while another class requires the fulfilment of physical constraints [21]. In this contest, the Perdew-Burke-Erzerhof (PBE) exchange-correlation functional [22] is a peculiar approach since it contains no fitted parameters. Nevertheless, the PBE generally provides results at least comparable to those obtained with more empirical functionals [23, 24]. The casting of PBE in a hybrid model, where a predefined amount of Hartree-Fock (HF) exchange is added self-consistently to the DFT contribution [25, 26, 27], leads to an even more accurate functional [25, 27, 28]. A number of tests have shown that by using this hybrid model, the calculated ionisation potentials, electronic affinities and a number of other electronic properties are remarkably close to experimental values [27, 29, 30].

In this work, we apply the PBE0 approach to correlate the reactivity of two different families of organometallic compounds toward the oxidation of two different electron donors.

The first family consists of a series of complexes of cobalt(II) with N$_4$-ligands (see Fig. 1), namely, Co(II) porphyrin (CoP), Co(II) phthalocyanine (CoPc), Co(II) teraphenylporphyrin (CoTPP), Co(II) tetrabenzoporphyrin (CoTBP) and Co(II) tetraazaporphyrin (CoTAP). These compounds are well-known as efficient catalysts for oxidative degradation of various types of pollutants and residual wastes [31, 32, 33, 34].

For a second example, we report the study of a class of Ru and Os compounds, namely M(bpy)$_2$L$_2$ complexes (M = Ru, Os, L = CN, SCN, bpy = 2,2'-bipyridine, see Fig. 2), which are the main components of photo-electrochemical cells that use dye sensitised semiconductor [35, 36, 37, 38, 39, 40, 41].

Despite a large number of experimental studies, the mechanism of the electrocatalytic processes involved in
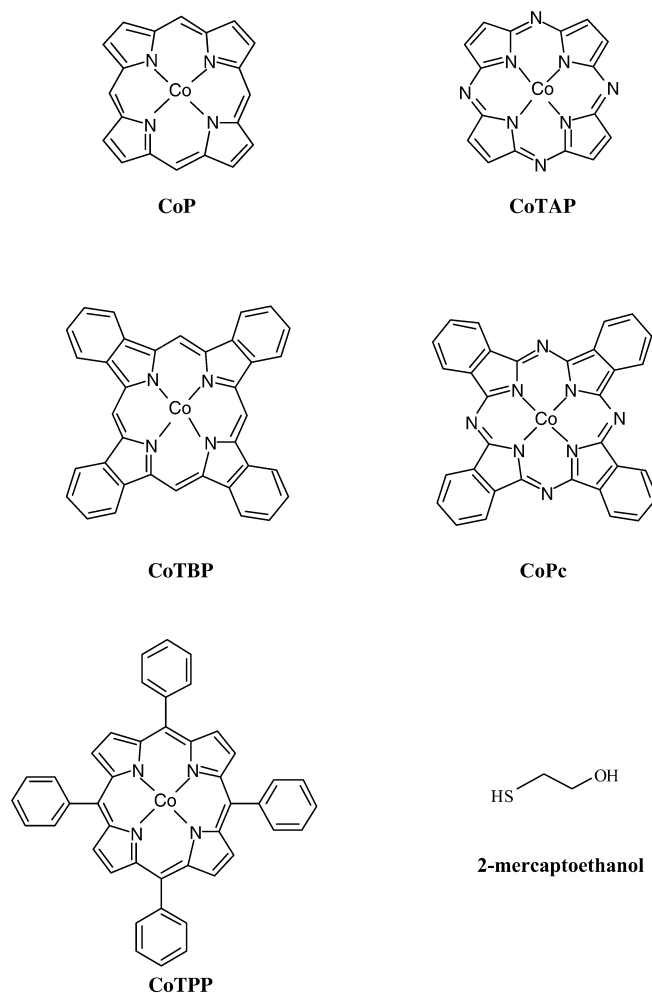
Fig. 1. Sketches of 2-mercaptoethanol and of the Co(II)-N$_4$ systems considered in the present paper: Co(II) porphyrin (CoP), Co(II) tetraphenylporphyrin (CoTPP), Co(II) tetrabenzoporphyrin (CoTBP), Co(II) tetraazaporphyrin (CoTAP), Co(II) phthalocyanine (CoPc)
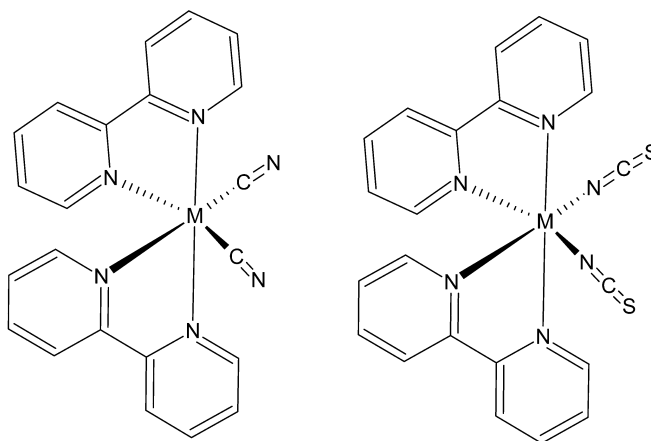
Fig. 2. Sketches of the Ru and Os complexes analysed

both families is not yet fully understood. Theoretical modelling could give some insights into the role of the ligands, of the metal atom (such as Os vs. Ru) and of the

chemical environment (the solution) on the observed experimental behaviour.

The final aim of this work is to relate the experimentally-observed differences in activity with the computed reactivity indexes (electrophilicity, intermolecular hardness) and to rationalise the different effects ruling such behaviour. Furthermore, since solvent could strongly modify the electronic properties of the systems, solute-solvent interactions were taken into account by introduction, into our Hamiltonian, of a continuum solvation model [42].

Computational details

All calculations were carried out with our modified version of the Gaussian 98 code [43], using a recent hybrid Kohn-Sham/Hartree-Fock (KS/HF) model referred to as PBE0 [28]. This approach is obtained casting the PBE exchange and correlation functional [22] in a hybrid scheme HF/DFT, where the HF exchange ratio (1/4) is fixed a priori [44].

All systems have been fully optimised at the PBE0 level, using the CEP-121 pseudopotentials and the corresponding basis set for the metal atoms, and the 6–31G(d) all-electron basis set for all of the other atoms [45]. All of the details about the optimised structures have been reported elsewhere [46, 47].

A larger basis set has been used for the computations of the reactivity descriptors, taking the 6–31+G(d,p) basis sets for the lighter atoms and adding one p polarization function (exp = 0.08) to the CEP-121 basis for the metal atoms. Unrestricted calculations were performed for the open-shell species.

Solvent effects were evaluated using the Polarizable Continuum Model (PCM) [42]. In particular, optimised structures and solvation energies have been computed by a cavity model, namely the United Atoms Topological Model (UATM) [48], coupled to the Conductor-like Polarizable Continuum Model (CPCM) [49]. This approach provides results very close to those obtained by the original dielectric model for high dielectric constant solvents, but it is significantly more effective in geometry optimisations, and less prone to numerical errors arising from the small part of the solute electron cloud lying outside the cavity (escaped charge effects) [49]. All CPCM calculations were performed in water.

The definition of the hardness (η) was given by Parr and Pearson [9, 10] and a three-point finite difference approximation leads to the following working definition:

$$\eta = (I - A) \quad (1)$$

where I and A are the first vertical ionisation potential and electron affinity of the neutral molecule, respectively. Analogously, the electronic chemical potential (μ) can be defined as:

$$\mu = -\frac{1}{2}(I + A) \quad (2)$$

Starting from these two quantities, the electrophilicity index (ω) was defined by Parr and co-workers [18] as:

$$\omega = \frac{\mu^2}{2\eta} \quad (3)$$

This expression may be regarded as a quantitative formulation of the model of Maynard et al., that introduced the concept of "electrophilicity power" of a ligand as a measure of its electron saturation [50].

Subsequently, the donor-acceptor intermolecular hardness (η_{DA}) can be defined as:

$$\eta_{DA} = (I_D - A_A) \quad (4)$$

where A_A is the electron affinity of the acceptor A (A here is the macrocyclic complex) and I_D is the vertical ionisation energy of the donor molecule D (D here is 2-mercaptoethanol or iodine) [51, 52]. This index compactly states the classical principle of electron transfer reaction, that the "transfer of electrons from D to A is faster the closer in energy the highest occupied molecular orbital (HOMO) of D is to the lowest unoccupied molecular orbital (LUMO) of A" [53]. It is important to mention that η_{DA} represents the hardness of the initial system (A + D) by considering the isolated acceptor and the donor species when the charge transfer has still not occurred, and therefore gives a general idea on their reactivity. Nevertheless, the intermolecular hardness as a reactivity index has been successfully used for the study of intermolecular charge transfer reactions of electrochemical interest (see for instance [54]). The extension of these indexes (ω, η) to the study of reactions involving open shell systems (like those considered here) is straightforward (see for instance [10, 12, 13]). Since Koopmans' theorem cannot be used unambiguously within the DFT framework, we have calculated the ionisation potentials and the electron affinities as the differences between the energies of the reference molecule (N electron system) and the corresponding $N+1$ or $N-1$ electron systems, at the geometry of the reference species. All of these latter calculations (the evaluations of the energies of the N, $N+1$ and $N-1$ electron systems) have been carried out with the 6-311+G(d,p) basis set for light atoms and the polarized CEP-121G basis for metal atoms.

Results and discussion

The electronic structure and all of the properties that can be derived from it (such as density, charges, electronic populations, ionisation potentials, electron affinities, and so on) fully characterize an isolated chemical system but only partially define its reactivity. Some simple symmetry rules, or more involved theories based mainly on the shape of the frontier orbitals, were derived to better model chemical reactivity at a relatively low computational cost (see for example [55]).

Within the framework of DFT, a more rigorous and chemically meaningful tool can be used to describe and interpret the selectivity of electron transfer reactions: the so-called *reactivity descriptors* or *indexes* [56]. These descriptors can be divided in two main classes: local and global indexes. The first class includes, for instance, the Fukui functions (see for instance [55]). These properties are highly desirable for establishing a reactivity-oriented description of molecular systems and, in particular, of different sites within a given molecule. On the other hand, global indexes, as hardness and softness [10], are characteristic of a system as a whole, and are therefore more suitable for comparison within families of similar molecules, as with those reported in the present paper. Among these latter indexes, the electrophilicity, ω, is an "intramolecular" parameter, depending only on the electronic characteristic of the acceptor species, while the hardness, η_{DA}, being defined on the acceptor and donor properties, is an "intermolecular" parameter. Therefore these two indexes together should give a complete picture of the electron transfer process.

N_4 complexes

The Co(II)-N$_4$ complexes were reported as efficient catalysts for the electrochemical oxidation of thiols [32, 33,

34]. In particular, modified electrodes coated with adsorbed or electropolymerised films made from these complexes have been extensively developed, as they act as electrocatalysts by lowering the overpotential of oxidation or reduction of the target molecules [34, 57]. Studies related to the electro-oxidation of thiols have shown that the catalytic activity of the adsorbed phthalocyanine-coated electrodes strongly depends on the nature of the central metal, with cobalt derivatives giving the best results [34]. More recent studies have extended the use of electropolymerized cobalt porphyrin film-coated electrodes to the electrocatalysis of the oxidation of thiols [58]. The cobalt porphyrin-modified electrode possesses a potential electrocatalytic activity for 2-mercaptoethanol electro-oxidation, but its activity is significantly lower than that of the phthalocyanine-based one. The reasons for the different chemical behaviours are still unclear. Here we have analysed five different complexes (CoP, CoPc, CoTPP, CoTBP and CoTAP, Fig. 1) to get a deeper theoretical understanding of reactivity.

Since ω quantifies the tendency of a molecule to "soak up" electrons, the higher it is, the greater the ability of the system to attract an electron from a generic donor molecule. The calculated values for the electrophilicity index (ω) for all of the five Co(II)-N$_4$ compounds in their optimised geometries are reported in Table 1. All of the complexes show comparable ω values, ranging from 2.0 (CoTAP) to 1.3 eV (CoTPP) but CoTAP has a ω value significantly higher than those for corresponding porphyrins (CoP and CoTPP). This is due to the electron-withdrawing effect of the additional nitrogen atoms in TAP. In contrast, CoPc and CoTBP have similar ω values, underlining the main role played by the benzene rings in storing electrons. Solvent strongly affects the magnitude of the calculated electrophilicities, but does not significantly alter the overall trend. In fact, in going from the gas phase to aqueous solution, CoTAP still has the highest ω value (3.6 eV) and CoTPP the lowest one (2.6 eV). The magnitude variations observed when going from gas to condensed phase are related to a strong change of the chemical hardness that significantly decreases from gas-phase to solution, while the chemical potential is much less affected [19]. This behaviour is due to the strong stabilisation of the cationic and anionic species in solution, which in turn rules the calculated I and A values: the first property decreases in going from gas-phase to solution, while the second increases. As a consequence the hardness augments due to the prevalence of the A term, while the chemical potential is less affected due to the opposite behaviour of the two quantities.

The computed electrophilicity indexes suggest that aza-porphyrins can accept electrons from a generic electron-donor more easily than the corresponding porphyrins and, consequently, they are predicted to be more active in the oxidation reaction of 2-mercaptoethanol. This trend is significantly enhanced by the interactions with a polar solvent such as water.

To explicitly take into account the role of the donor molecule in the electron transfer process we have to consider the intermolecular donor-acceptor hardness (η_{DA}), as defined by Eq. 4. The η_{DA} values for the whole series of N$_4$ macrocycles are plotted in Fig. 3. We recall that the smaller the value for the hardness, the greater are the interactions between donor and acceptor species, since this corresponds to a small energy gap between the donor HOMO orbital and the LUMO of acceptor. From the analysis of our gas phase values we can observe that the porphyrin-like macrocycles (CoP, CoTBP, and CoTPP) are predicted to be the most reactive species towards 2-mercaptoethanol, all showing similar η_{DA} (about 2.4 eV). Higher hardness values are found for the aza-compounds, CoPc and CoTAP, (3.0 and 3.2 eV, respectively) predicted to be less reactive, contrary to our gas phase results obtained by considering the electrophilicity index (ω). This result can be rationalised in terms of the relative energies of the donor and acceptor orbitals. In fact, the electron-withdrawing substituent (the additional nitrogen atom in aza-porphyrins) of the macrocycles significantly stabilises the SOMO, whereas the contrary is true for the electron-donating substituent (the methylene group). Since the HOMO of the thiol is quite high in energy, CoTAP and CoPc show greater hardness [47].

Solvent has a drastic effect on the intermolecular hardness. The η_{DA} for CoP and CoTBP change from 2.4 to 3.2 eV in going from gas-phase to aqueous solution, and more interestingly, similar variations, but in the opposite directions, can be found for the aza-compounds. It is also noteworthy that CoTAP is predicted to be slightly more reactive than CoPc (2.4 vs. 2.6 eV).

Two main effects are responsible for these results. First of all, the anion of 2-mercaptoethanol, being a charged species, is strongly stabilised by the solvent and the energy of its HOMO significantly drops. At the same time, aza-porphyrins are more polarisable than porphyrins (having higher dipole moments), so that they strongly experience the reaction field generated by the continuum. The net effect is a complete inversion of the prediction in going from the gas-phase to the aqueous solution.

In summary, the two reactivity indexes (ω and η_{AD}) provide complementary information about the reactivity of the different species. In fact, both indexes point out that in solvent aza-porphyrins are more reactive than the

Table 1. Electrophilicity index (ω, eV) of the Co(II)-N$_4$ systems. The values have been calculated both in the gas-phase and in aqueous solution at the corresponding optimised geometries

Molecule	Gas-phase	Solution
CoTAP	2.0	3.6
CoP	1.5	2.7
CoTPP	1.3	2.6
CoPc	1.8	3.2
CoTBP	2.0	3.1
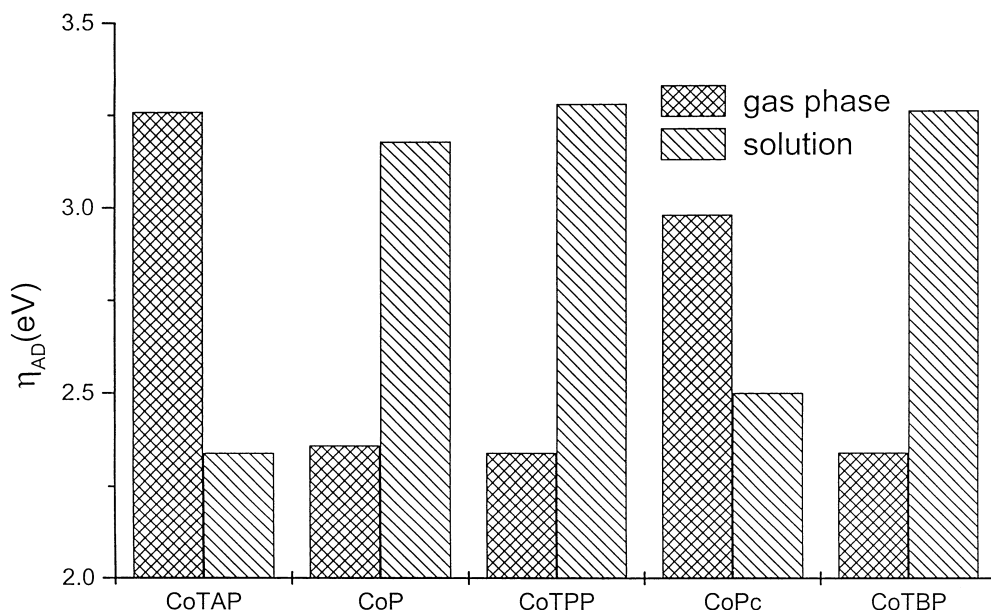
Fig. 3. Plots of the intermolecular donor-acceptor hardness (η_{AD}, eV) in the gas-phase and in aqueous solution for the five Co(II)-N$_4$ systems. See Fig. 1 caption for the acronyms

corresponding porphyrins, due to the presence of the electronegative (and more polarisable) nitrogen atoms in the inner ring. Nevertheless, the electrophilicity index alone does not allow for unambiguous discrimination between the different species. At the same time, bulk solvent effects control to some extent the reactivity of such species, even in the absence of any specific solute-solvent interactions. Recently some experimental investigations on the reaction kinetics of the electrocatalytic oxidation of 2-mercaptoethanol (2-ME) by adsorbed CoTPP and CoPc on vitreous carbon electrode in aqueous solution were carried out [47]. A good correlation between the measured apparent rate constant (k, in log scale) and the chemical hardness η_{DA} (computed taking into account bulk solvent effects) was found [47], underlining the possibility of using this index to predict reactivity.

Ru and Os complexes

The Ru and Os polypyridyl complexes used for the second test case are one of the main components of photoelectrochemical cells that use dye sensitised semiconductors [36, 37]. These cells consist of a dye, present as a monolayer at the interface between a semiconductor surface (usually mesoporous TiO$_2$) and an electrolyte containing a redox pair. In such systems, photons are absorbed by the dye, and the excited electron is injected very quickly into the semiconductor while the dye is regenerated by a redox pair such as I$^-$/I$_3^-$. Working principles of these devices have been exposed in many articles and reviews [38]. The peculiar molecular properties of the dyes, and the possibilities of related technological applications, are, among others directly related to a fast and efficient regeneration of the dye cation after the electron injection; that is an efficient reduction of the

dye cation from the iodine in solution. This last point is of crucial importance for a high rate of light-to-electric energy conversion [36, 38].

Here we have focused on the Ru and Os polypyridyl complexes *cis*-M(bpy)$_2$(NCS)$_2$ and *cis*-M(bpy)$_2$(CN)$_2$, which have attracted much interest due to their extremely high light-to-energy conversion (up to 15%) [38, 39, 40]. The calculated values of the electrophilicity indexes for four such complexes are reported in Table 2. Since we are interested in the regeneration of the dye *after* electron injection, these descriptors have been computed only for the cationic species.

All of the polypyridyl complexes show comparable ω values in the gas phase, ranging from 6.9 ([*cis*-Os(bpy)$_2$(CN)$_2$]$^+$) to 7.6 eV ([*cis*-Os(bpy)$_2$(NCS)$_2$]$^+$), suggesting similar behaviour toward reduction. The general trend is preserved in going from the gas-phase to aqueous solution, [*cis*-Os(bpy)$_2$(NCS)$_2$]$^+$ still having the highest ω value (9.2 eV) and [*cis*-Os(bpy)$_2$(CN)$_2$]$^+$ the lowest (7.4 eV). Nevertheless, the two thiocyanide compounds have much larger ω than the corresponding cyanides, so they should have a greater electron-accepting ability. This fact reflects the greater polarisability of the SCN group with respect to CN. As in the case of Co(II)-N$_4$ complexes, the variations observed in

Table 2. Electrophilicity index (ω, eV) of the Ru/Os complexes. The values have been calculated both in the gas-phase and in aqueous solution at the corresponding optimised geometries

Molecule	Gas-phase	Solution
RuNCS	7.2	8.8
RuCN	7.1	7.7
OsNCS	7.6	9.2
OsCN	6.9	7.4

condensed phase are related to a strong change in the chemical hardness, the chemical potential being practically unaffected when going from gas-phase to solution [19].

Furthermore, on the basis of our calculations, the Os compounds should be as active as the corresponding Ru derivatives. While this last trend is experimentally observed, the CN derivatives are regenerated faster than the SCN ones after irradiation. This fact suggests a greater capacity as electron acceptors [5] of the CN complexes, contrary to our predictions based on the electrophilicity index.

Once again, to better understand the reasons for this discrepancy, we have analysed the electron transfer process in terms of the intermolecular donor-acceptor hardness (η_{DA}) computed in gas-phase and in solution, when the donor is the I^- anion and the acceptors are the Ru or Os complexes. The η_{DA} values for the whole series of polypyridyl systems are plotted in Fig. 4. The striking feature of Fig. 4 concerns the negative values of all gas-phase η_{DA}, the data ranging between −3.6 and −3.2 eV. These results indicate that, in the gas-phase, the reactivity is largely dominated by the electron affinity of the acceptor molecules (the polypyridyl complexes). We can also observe that the CN complexes are predicted to be the most reactive species, all showing similar η_{DA} (about −3.5 eV). Higher hardness values are instead found for the thiocyanide species (about –3.2 eV). The rationalisation in terms of the energy of the empty frontier orbital of the acceptor species is straightforward: the LUMO orbital of the cationic species containing SCN has partial metal-ligand antibonding character and therefore lies higher in energy than the corresponding orbital of the cyanide complexes. As a consequence, the electron affinity is lower for the first species than for the second one.

Solvent has a drastic effect on the hardness, inducing a significant increase in all computed values (Fig. 4). In particular, the η_{DA} for the cyanide species rises from about −3.5 eV to about 0.1 eV for the Ru complex and to 0.3 eV for the Os compound in going from the gas-phase to aqueous solution. An even more drastic effect has been found for cyanide systems, the increase being of about 3.9 eV.

The changes in η_{AD} observed when going from gas-phase to solution can be rationalised in a similar way as done for Co(II)-N_4 complexes: a stabilisation of the iodine HOMO and a larger polarisability of cyanide with respect to thiocyanide.

On the other hand, in contrast to the behaviour found for the two N_4-complexes, the trend in going from the gas-phase to the solution is preserved, even if a significant increase of η_{AD} has been found. The differences between cyanide and thiocyanide complexes containing the same metal atom are nevertheless increased. It is interesting to note that the electron withdrawing groups (SCN), although decreasing the electron density on the metal centre, also contribute to increasing the gap between the energy of the LUMO of the acceptor and the HOMO of the donor, reducing the reactivity (increasing η_{DA}).

The reactivity of the complexes with I^- predicted from the computed intermolecular hardness is in agreement with the experimental data (RuCN > OsCN > RuNCS > OsNCS) [39, 40]. However, in the case of *cis*-Os(bpy)$_2$(NCS)$_2$, a particularly low reaction rate was experimentally found, while the computed η_{DA} is not very different from that of the corresponding Ru complex (0.23 eV). Furthermore, other experiments carried out on the cyanide complexes [39] found a sluggish reaction rate with the *cis*-Os(bpy)$_2$(CN)$_2$ complex, in contrast to more recent results [41]. These latter
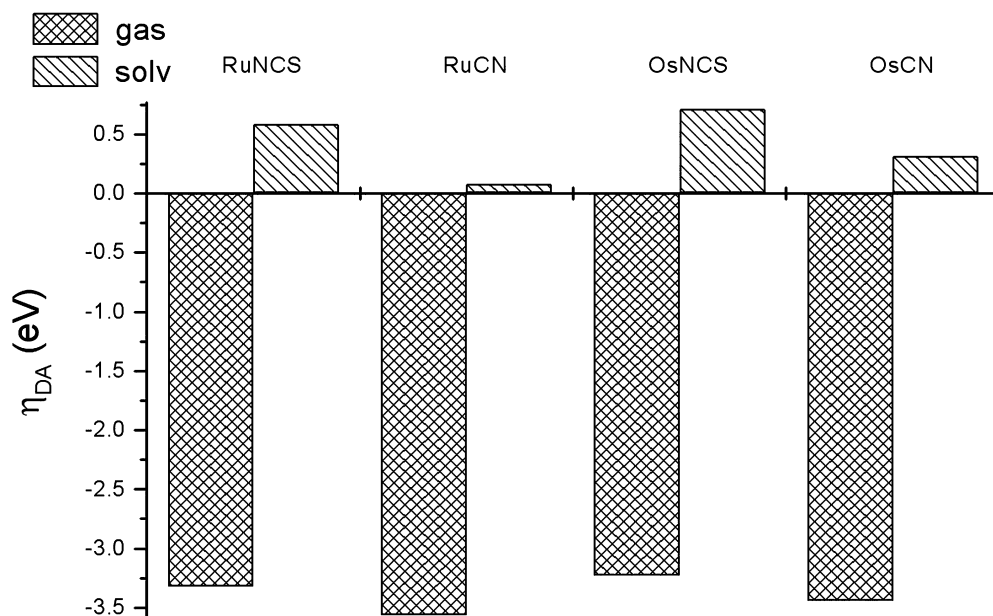
Fig. 4. Plots of the intermolecular donor-acceptor hardness (η_{AD}, eV) in the gas-phase and in aqueous solution for the Ru/Os systems. In the plot OsCN stands for Os(bpy)$_2$(CN)$_2$, RuCN for Ru(bpy)$_2$(CN)$_2$, OsNCS for Os(bpy)$_2$(CN)$_2$ and RuNCS for Ru(bpy)$_2$(NCS)$_2$

194

contradictory experimental results suggest that additional experimental parameters (TiO$_2$ band edge position, dye adsorption, and so on) may strongly affect the measured reaction rates.

Conclusions

In this paper, a recent DFT method (the PBE0 model) was applied to analyse the reactivity of two different classes of electrochemically interesting compounds, namely the Co(II)-N$_4$ complexes and some Ru(II)/Os(II) polypyridyl complexes. Intermolecular hardness and electrophilicity indexes have been used to investigate their reactivity towards electron donors such as 2-mercaptoethanol and iodine, both in the gas-phase and in aqueous solution.

Our results suggest that the electrophilicity index alone cannot be used to discern the reactivity of an acceptor towards a specific donor, and that the intermolecular hardness should also be taken into account.

Furthermore, the effect of the solvent is extremely important for these reactions that involve charged and polarisable species. The CPCM model, although taking into account only non-specific solute-solvent interaction, has been demonstrated to correctly reproduce the bulk effects.

Finally, the main result of this study is that reactivity indexes can be considered as reliable tools in the prediction of the reactivity trends, provided that a realistic electronic simulation, including environmental (solvent) interactions is performed.

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