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The Standard Redox Potential in the Study of Solute–Solvent Interactions. Dirhodium Complexes

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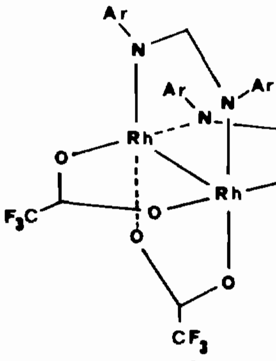
Abstract

A wide series of empirical parameters of solvents are employed in the study of the dependence of the redox potentials of some dirhodium(II) derivatives [namely, $Rh_2(O_2CCF_3)_2(form)_2$, $Rh_2(form)_4$, $Rh_2(ONHCF_3)_4$] upon the solvent nature. A statistical approach is proposed which analyzes the influence of solvent basicity, acidity and polarizability both independently and jointly. This has proved to be useful in rationalizing the solvent effects on the redox potentials, as well as in suggesting different solvation models.

Introduction

The problems involved in the wide field of solute–solvent interactions vary in nature with respect to both the context in which they arise and the techniques employed in their study. Despite the restrictions imposed by the relatively narrow range of suitable solvents and by the request of a high enough reversibility degree of the charge transfer involved in the measurement, electrochemistry can contribute to this kind of problem. In this context, we have previously dealt with the role of the solvent in conditioning the redox potential of the couple UO_2^{2+}/UO_2^{+} [1], making a proper use of empirical scales of solvent basicity, acidity and polarizability, through a statistical data treatment involving both single- and multiparameter regression analyses [2]. Our aim is now to apply this type of investigation to the study of the solution chemistry of coordination compounds. As a first, limited benchmark to check the capability of this approach in the case of more complicated molecules, we report here on the results obtained with the dirhodium(II) complexes $Rh_2(form)_2(O_2CCF_3)_2$ [3], compound **1**; $Rh_2(form)_4$ [4], compound **2** (form = *N,N'*-di-*p*-tolylformamidinate anion); and $Rh_2(ONHCCF_3)_4$ [5], compound **3**; all bearing basically the same 'lantern' structure.

In all the complexes the metal–metal centre exhibits free axial coordination sites, so that they can



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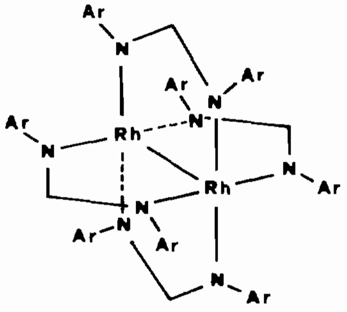

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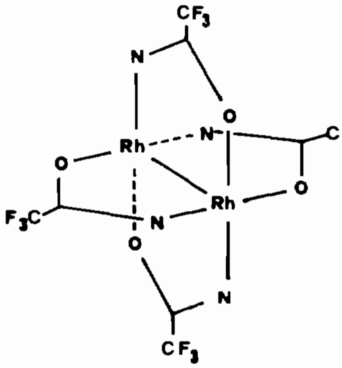

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Ar = CH_3-p-C_6H_4

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potentially form mono- and bis-adducts with Lewis bases. On the other hand, the electronic properties of the ligands are markedly different.

The electrochemical behaviour of derivatives **1**–**3** in nonaqueous solvents has been described elsewhere [3–5]. We recall here that all these complexes undergo two distinct one-electron oxidation processes according to the sequence

$$\mathrm{Rh(II)–Rh(II)} \underset{+e^-}{\overset{-e^-}{\rightleftharpoons}} \mathrm{Rh(II)–Rh(III)}$$

$$\mathrm{Rh(II)–Rh(III)} \underset{+e^-}{\overset{-c^-}{\rightleftharpoons}} \mathrm{Rh(III)–Rh(III)}$$

While the first anodic step consists in a simple reversible charge transfer, the second charge transfer is complicated by following chemical reactions which make Rh(III)–Rh(III) unstable. In the present paper we will refer to the standard potential of the redox couple Rh(II)–Rh(III)/Rh(II)–Rh(II).

Experimental

By cyclic voltammetric tests on the first reversible redox process it is possible to evaluate $E^r_{1/2}$ for the couples Rh(II)–Rh(III)/Rh(II)–Rh(II). $E^r_{1/2}$, the reversible half-ware potential, is computed as $(E_{p,a} + E_{p,c})/2$, where $E_{p,a}$ and $E_{p,c}$ are the anodic and cathodic peak potentials of the recorded anodic–cathodic peaks system, respectively. The quantity computed by this procedure is an excellent estimate of the standard redox potential [6]. It is referred to $E^r_{1/2}$ of the couple bis-cyclopentadienyliron(III)/iron(II), measured on the same solutions, in order to remove variable liquid junction potentials [7].

The solvents considered are (i) compound **1**: dichloromethane, acetonitrile, acetone, nitromethane, *N,N*-dimethylformamide, benzonitrile, tetrahydrofuran; dimethylsulphoxide [3]; (ii) compound **2**: dichloromethane, acetonitrile, *N,N*-dimethylformamide, tetrahydrofuran, pyridine [4]; (iii) compound **3**: acetonitrile, acetone, nitromethane, *N,N*-dimethylformamide, benzonitrile, tetrahydrofuran, n-butyronitrile [5]. All data are at a temperature of 20 °C.

The following empirical solvent scales are considered: $E_T(30)$, the Reichardt parameter [8]; *AN*, the Gutmann acceptor number [9]; *Z*, the Kosower value [10]; χ_R and χ_B, the Brooker scales [11]; A_N, the Knauer–Napier parameter [12]; *S*, the Brownstein scale [13]; α, π^* and β, the Kamlet–Taft solvatochromic parameters [14]; *DN*, the Gutmann donor number [9]; *B*, the Koppel–Palm parameter as refined by Shorter [15]; $\Delta\nu_D$ and $\Delta\nu_A$, the Kagiya solvent electron-donating and electro-accepting power, respectively [16]; *PA*, the solvent proton affinity [17]; *EH*, the Bontempelli $E^r_{1/2}$ value for the couple H^+/H_2 [18]. It is worth recalling that $E_T(30)$, *AN*, χ_R, χ_B, A_N, *S* and α are acidity parameters; β, *DN*, *B*, $\Delta\nu_D$, $\Delta\nu_A$, *PA* and *EH* are basicity parameters, while π^* is a polarity–polarizability parameter.

The statistical treatment of the data consists in single and multiple regression analyses. t-Tests and F-tests are performed in order to compute the level of significance in verifying the proper null hypothesis [19, 20].

Results and Discussion

Table 1 reports the results of the single parameter regression and correlation analyses, limited to the cases where the significance of the regression coefficients results at least 0.1. It can be noted that for compound **3** several simple linear regressions with basicity parameters satisfactorily account for the changes in the redox potential values. Less satisfactory results are found in the case of compound **1**, and no really acceptable correlation can be found for compound **2**. In all cases the redox potential results uncorrelated with parameters which account for the acidity of the solvent.

TABLE 1. Results of Simple Linear Regression Analyses[a]

Compound	Independent variable, slope and level of significance	Intercept	$\lvert r \rvert$	*l*
1	β: −0.2673(0.05)	0.2543	0.7954	6
	DN: −0.0063(0.005)	0.2340	0.8866	8
	B: −0.0013(0.005)	0.2860	0.8699	8
	$\Delta\nu_D$: −0.0013(0.005)	0.2147	0.8652	8
	EH: 0.1867(0.025)	0.2009	0.9011	5
2	*DN*: −0.0047(0.10)	−0.2354	0.7242	5
3	β: −0.6673(0.005)	0.9117	0.9714	5
	DN: −0.0130(0.0005)	0.8136	0.9565	7
	B: −0.0028(0.005)	0.9377	0.9601	6
	EH: 0.4730(0.005)	0.7908	0.9972	4
	$\Delta\nu_A$: 0.0375(0.10)	0.5804	0.9618	3

[a] *r* = correlation coefficient; *l* = number of observations.

It is evident that the main solvent effect must be ascribed to the coordination of solvent molecules to the metal, as axial ligands. If the only interaction is a σ-type interaction between the Lewis acid metal centres and the Lewis base solvent molecules, one will expect that a typical basicity scale, such as *DN*, accounts for the solvent effect on the redox potential. Increasing the basic strength of the solvent,

TABLE 2. Results of Multiparameter Regression Analyses

Compound	Independent variables, coefficients and level of significance	Intercept	r^2	l	Level of significance of addition of the variable indicated
1	β: −0.2687(0.005); $E_T(30)$: −0.0108(0.01)	0.7177	0.9653	6	$E_T(30)$(0.10)
	EH: 0.2018(0.005); $E_T(30)$: −0.0078(0.025)	0.5469	0.9864	5	$E_T(30)$(0.10)
	β: −0.4249(0.01); A_N: −1.1994(0.025); π^*: −0.8127(0.025)	18.3717	0.9999	5	π^*(0.05)
2	β: 0.2502(0.05); χ_R: 0.0657(0.025)	−3.4384	0.9973	4	χ_R(0.10)
	β: −0.1627(0.1); A_N: 0.0657(0.025)	8.1850	0.9948	4	A_N(0.10)
	B: −0.0009(0.01); $E_T(30)$: −0.0192(0.01)	0.5984	0.9833	5	$E_T(30)$(0.05)
	DN: −0.0052(0.025); $E_T(30)$: −0.0167(0.025)	0.4686	0.9657	5	$E_T(30)$(0.10)
	DN: −0.0049(0.01); Z: −0.0087(0.025)	0.3305	0.9997	4	Z(0.05)
	DN: −0.0051(0.01); S: −0.7119(0.025)	−0.3642	0.9995	4	S(0.10)
	$\Delta\nu_D$: −0.0010(0.01); $E_T(30)$: −0.0189(0.01)	0.5465	0.9790	5	$E_T(30)$(0.10)
	EH: 0.1677(0.025); $E_T(30)$: −0.0170(0.025)	0.4683	0.9967	4	$E_T(30)$(0.10)
	DN: −0.0047(0.005); $E_T(30)$: −0.0108(0.01) π^*: −0.2006(0.01)	0.3757	1.0000	5	π^*(0.05)
	DN: 0.0032(0.025); A_N: 1.1143(0.01) π^*: −1.5807(0.01)	−16.5186	0.9999	5	π^*(0.05)
	β: −0.0654(0.005); π^*: −0.5025(0.0005)	0.0874	1.0000	4	π^*(0.05)

As an example, the first regression equation should be written as: $E^r_{1/2} = -0.2687\beta - 0.0108E_T(30) + 0.7177$. r = correlation coefficient; l = number of observations.

a stronger solvent binding ability of the Rh(II)–Rh(III) in respect to the Rh(II)–Rh(II) species leads to a stabilization of the higher oxidation state and to a consequent cathodic shift of potential. In this context, the capability of a basicity scale of explaining the trend of the $E^r_{1/2}$ values, or, on the other hand, the need of involving also an acidity scale, can be taken as an indication of the kind of solute–solvent interactions actually involved.

Table 2 reports the results of linear multiparameter regression analyses, only for those cases where the coefficients are significant to at least the 0.1 level (t-test) and, at the same time, the addition of acidity or polarizability to basicity terms in the regression equation is significant to at least the 0.1 level (F-test).

A comparison between the data in Tables 1 and 2 indicates the effectiveness of the statistic instrument adopted and provides useful suggestions about how to link the data with the chemical problem. In point of fact, for compound **3** the use of additional acidity or polarizability parameters does not improve the results obtained using only basicity scales, which, in this case, by themselves satisfactorily account for the effect of the solvent. On the other hand, the use of acidity parameters appears to be of primary importance in the case of compound **2**, when completely unsatisfactory results are obtained with any single basicity scale. For this compound, not only the addition of an acidity parameter is quite often significant, but it also leads to very good linear relationships which account for the experimental results quite well. In some instances further addition of the polarizability parameter π^* leads to a still better fit.

As an intermediate case, the behaviour of compound **1**, which is to some extent accounted for simply by basicity scales, can be better explained by some particular combinations of basicity and acidity parameters.

The consideration that, even if only to some extent, the behaviour of the three complexes studied can be explained considering only basicity parameters, and by no means only acidity scales, is not surprising taking into account that, as mentioned above, the complexes are Lewis acids [21], so allowing a σ interaction of the solvent molecules with the metal–metal centre along the free axial positions [22]. For all the computed simple regressions the absolute value of the slopes of the regression lines on the different basicity scales are in the following order: compound **3** > compound **1** > compound **2**. This suggests that the corresponding mixed-valent Rh(II)/Rh(III) species are stabilized, in respect to the starting Rh(II)–Rh(II) dimers, to an extent varying in this order, if only σ interactions are considered. However, the results of the regression analyses suggest that this simple assumption is inadequate. On the other hand, although in the well known carboxylate derivatives the interactions with the axial ligands have been mainly interpreted in terms of σ-type interaction, calorimetric measurements on the formation enthalpies of mono- and bis-adducts of the complex $Rh_2[O_2C(CH_2)_2CH_3]_4$ could be accounted for considering both σ-interaction and π-stabilization [23]. The ability of the Rh_2^{4+} complexes to act as π-donors was also recently evidenced by IR data on the complexes $Rh_2(O_2CCH_3)_n(HNOCCH_3)_{4-n}(CO)_x$, where $n = 0$, 4 and $x = 1, 2$ [24] and $Rh_2(form)_4(CO)$ [4] – just compound 2, for which basicity scales seem inadequate in the context of the present paper. These compounds show a significant shift towards low frequencies of the $\nu(CO)$ bands with respect to the carboxylate derivatives, in accord with a significant π-backbonding. In agreement with these findings, even if the bulkiness of the ligand does not constitute the main factor, DV-X_α calculations and UV-PE spectra on the series $Rh_2(O_2CCF_3)_n(form)_{4-n}$ [$n = 0$ (compound 2), $n = 2$ (compound 1), $n = 4$)] [25] give evidence for a gradual significant destabilization of the HOMO as the number of the formamidinato groups increases. This implies a greater π-donor ability of compound 2 with respect to compound 1. In addition, the destabilization of the σ^* LUMO of compound 2 with respect to compound 1 causes a lower interaction between the lone pairs of the eventual donors and this orbital because of their poor energy matching. The same conclusions can be drawn by considering the $\nu(CO)$ frequencies in the carbonyl complexes $Rh_2(form)_2(O_2CCF_3)_2(CO)_n$ ($n = 1, 2$; $\nu(CO) = 2090$ cm^{-1}) [26] and $Rh_2(form)_4(CO)$ ($\nu(CO) = 2040$ cm^{-1}) [4]; the shift towards lower frequency values supports the greater π-donor ability of compound 2.

Hence, our findings about the types of solute–solvent interaction agree with data collected for these and similar compounds in studies involving measurements of a completely different nature. Multiple regression analysis of redox potentials proves to be an effective tool not only in finding the most suitable equations to account for the dependence of this thermodynamic parameter on the nature of the solvent, but also in gaining information about the kind of solute–solvent interactions and on the electronic effects inside the molecule of the species studied.

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