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An EPR investigation of the thermodynamics and kinetics of a reversible intramolecular metal–ligand electron transfer in rhodium complexes *

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Abstract

The temperature dependence of a reversible intramolecular metal–ligand electron transfer for a series of semiquinone-rhodium(I) complexes in equilibrium with their catecholate-rhodium(II) isomers has been investigated by EPR spectroscopy, in a wide range of solvents. Both the thermodynamics and kinetics of this process are reported, along with a discussion of the role of the solvent and of the electronic and molecular structure of the complexes.

We have previously communicated [1] data concerned with the reversible intramolecular metal–ligand electron transfer in the reactions of (1,2-semiquinone)-rhodium(I) complexes with $AsEt_3$ or PPh_3 (eq. 1). The phenomenon of redox-isomerism taking place for some pentacoordinate rhodium complexes also has been reported (eq. 2),

$$[L_2Rh^{I}(sq)] + L' \rightleftharpoons [L_2L'Rh^{II}(cat)] \quad (1)$$

$$[(cod)(Et_3As)Rh^{I}(sq)] \rightleftharpoons [(cod)(Et_3As)Rh^{II}(cat)] \quad (2)$$

where L = PPh_3 and $\frac{1}{2}$cod; cod = cycloocta-1,4-diene; L' = $AsEt_3$ or PPh_3; sq = 1,2-semiquinone, cat = the catecholate dianion of the corresponding 1,2-quinone.

The electronic structure of the square-planar complexes $[L_2Rh(sq)]$ and its influence on the possibility of intramolecular electron-transfer (IMET) in the reaction has been analyzed in detail elsewhere [2,3]. The band frequency of the metal–ligand charge-transfer ($d_{z^2} \rightarrow \pi^{\star}_{sq}$) transition in the electronic spectra of the complexes $[L_2Rh(sq)]$ was also shown to be the practical criterion defining the occurrence of IMET when $AsEt_3$ was added to these complexes [3].

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* Dedicated to Professor Colin Eaborn in recognition of his important contributions to organometallic chemistry.

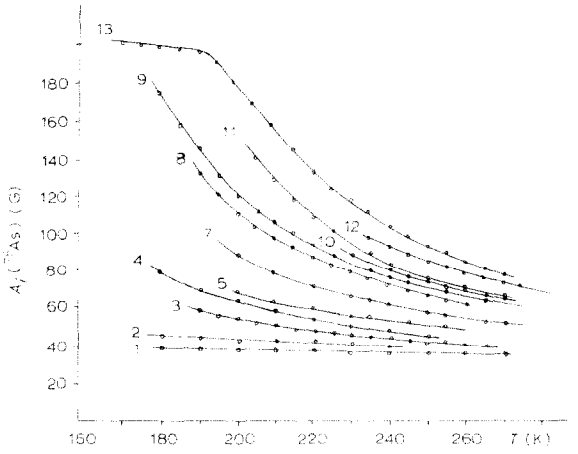

Fig. 1. $A_i(^{75}As)$ dependence in the EPR spectra of complex **2** upon temperature: the numbers correspond to the solvents listed in Table 2.

The present work describes an EPR study of the thermodynamics and kinetics of the redox-isomerism equilibrium for the rhodium complexes [(cat)(Et_3As)Rh^I(sq)], **1**–**4**, in which sq and cat are the appropriate monoanion or dianion derivatives of the following 1,2-quinones: 3,6-di-t-butyl-4-methoxy-benzo-1,2-quinone (**1**), 3,6-di-t-butylbenzo-1,2-quinone (**2**); 3,5-di-t-butyl-6-chlorobenzo-1,2-quinone (**3**); and 3,6-di-t-butyl-5-chlorobenzo-1,2-quinone (**4**). Besides the influences of the sq-ligand and the nature of the solvent on equilibrium 2, the possible stereochemistry of redox-isomers and the factors defining the presence of redox-isomerism of transition metal complexes with free-radical ligands are discussed in this paper.

Experimental and discussion

Temperature dependence of the EPR spectra

The isotropic EPR spectra of complexes 1/2 are 1/1/1/1 quartets due to the interaction of the unpaired electron with the ^{75}As nucleus ($I = 3/2$). Unlike complexes [(cod)(Et_3As)Rh(sq)] (**5**: q = 3,6-di-t-butyl-4,5-dimethoxybenzo-1,2-quinone and **6**: q = 1,4,5,6,7,8-hexachloroxanthine-2,3-quinone), whose EPR spectra do not change with temperature and solvent variation, the EPR spectra of the complexes **1**–**4** depend on both solvent and temperature. The character of the $A_i(^{75}As)$ and g_i temperature dependence is the same for all four complexes, in all solvents used: both parameters increase as the temperature decreases. However, the rate of the $A_i(^{75}As)$ and g_i changes as a function of temperature depends on both the quinone and the solvent (Fig. 1).

The change of isotropic EPR spectral parameters with decreasing temperature is accompanied by an unsymmetrical widening of the components of the quartet spectrum, down to their final disappearance (Fig. 2). For complex **2** in CH_2Cl_2 and the complex **3** in toluene, a new four-component EPR spectrum was observed at low temperature (in liquid solvents), whose components are unsymmetrically narrowed with further cooling.

Table 1

EPR spectral parameters for the complexes **1–6** in toluene at 260 K

Complex	g_i	$A_i(^{75}As)$ (G)
1	2.0020	26.8
2	2.0380	21.6
3	2.0500	24.8
4	2.0410	22.8
5	2.0019	26.3
6	2.0690	237.0

The changes observed represent a typical picture for fast (relative to EPR time scale) reversible transitions between two isomeric forms of paramagnetic complexes which are differentiated by their values of A_i and g_i [4]. The low temperature EPR spectra of **2** in CH_2Cl_2 and **3** in toluene show that one of the forms taking part in the exchange reaction is the catecholate rhodium(II) complex, being analogous to complex **4**. In comparison to the semiquinone complexes (for example **5**), the catecholate derivatives have greater values of g_i and $A_i(^{75}As)$ (see Table 1). The values of isotropic EPR spectra parameters for the catecholate isomers of **2** and **3** conform well with the parameters from their anisotropic EPR spectra in glassy matrices at 77 K. Both the axial symmetry of the $\bar{g}$- and $\bar{T}$-tensors and values of $g_x = g_y$ correspond to a ground state with a molecular orbital (MO) consisting of the Rh d_{z^2} orbital and an As(sp^n) hybrid orbital [3].

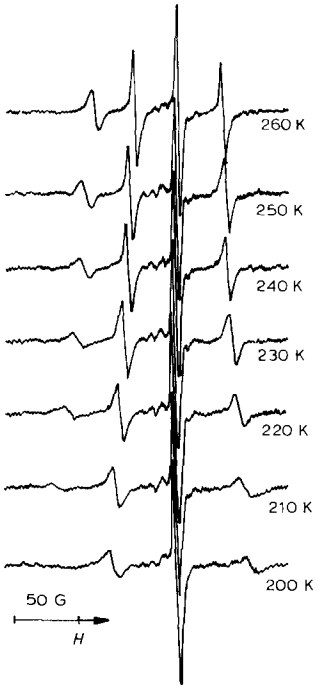

Fig. 2. The appearance of the EPR spectrum for **3** in 2-methylbutane at different temperatures.

The isotropic EPR spectra for the second isomeric forms of **1**–**4** were not observed. There are three principal reasons for this: firstly, the low-equilibrium concentration; secondly, the small lifetimes, leading to additional broadening of the EPR spectral components; thirdly, the overlapping of the EPR spectrum of the semiquinone isomer with the components of that for the catecholate isomer. However, there are components corresponding to the semiquinone isomer in the anisotropic EPR spectra of complexes **1**–**4** in the $g \approx 2.000$ region. The small value of $A(^{75}As)$ and the absence of appreciable anisotropy for the g and T-tensors from these spectra are characteristic of semiquinone complexes, for example **4**, unambiguously indicating that their structure is with the unpaired electron on the ligand [3]. Thus, complexes **1**–**4** exist in solution as two isomers which interconvert rapidly. In glassy matrices, conformational transitions are slowed down and both isomers are observed in the EPR spectra.

Thermodynamics for the redox-isomerism equilibrium

The temperature dependence of the redox-isomerism equilibrium (eq. 2), as displayed in the changing $A_i(^{75}As)$ values, allows the determination of thermodynamic parameters from this process. The equilibrium constant for eq. 2 is given by eq. 3

$$K = \frac{P}{(1-P)} \tag{3}$$

where P is the mole fraction of the catecholate isomer, and $(1-P)$ is the mole fraction of the semiquinone isomer. The magnitude of the experimentally observed A constant for the hyperfine coupling (HFC) with the ^{75}As nucleus will be dictated by eq. 4 under conditions of fast exchange,

$$A = PA_{cat} + (1-P)A_{sq} \tag{4}$$

where $A_{cat} = A_i(^{75}As)$ for the catecholate isomer and $A_{sq} = A_i(^{75}As)$ for the semiquinone isomer. To obtain the expression connecting the equilibrium constant K with A, expressions 3 and 4 are manipulated to give eq. 5.

$$K = \frac{A - A_{sq}}{A_{cat} - A} \tag{5}$$

The K values calculated by eq. 5 at different temperatures have been used for the definition of the thermodynamic parameters for the redox-isomerism equilibrium. Figure 3 demonstrates the $\ln(K)$ dependence on $1/T$ for **2** in different solvents. ΔH° and ΔS° values for **2** and **3** are given in Table 2. The comparison of the data obtained indicates that in all cases, independent of the nature of the ligand and the solvent, the enthalpy of the redox-isomerism equilibrium (in the form written in eq. 2) is negative. That is, discounting the entropy, the redox-isomerism equilibrium has to be always displaced towards the catecholate complex. However, the entropy also reduces when passing from the sq- to the cat-isomer; that is, the semiquinone isomer is entropically more advantageous. This change in the entropy with temperature compensates for the difference in enthalpy. Hence, in so far as the absolute significance of ΔH° is small ($|\Delta H^\circ| \leqslant 13$ kJ mol^{-1}), the temperature change influences critically the ΔG values of the reaction. Thus, at low temperatures, ΔG° is negative: increasing the temperature changes the sign of ΔG° to positive at a

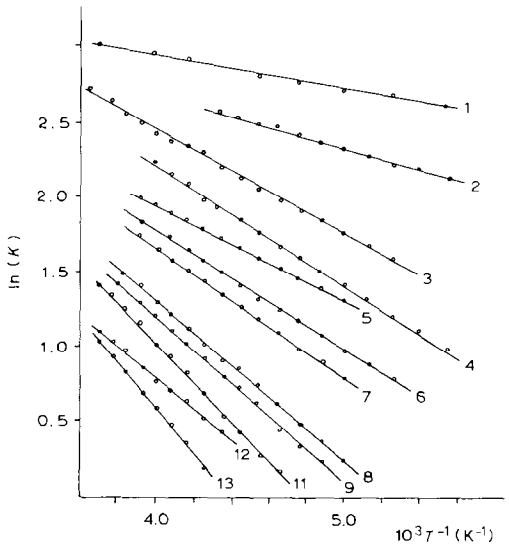

Fig. 3. The ln(K) dependence on $1/T$ for complex **2** in different solvents. The numbers correspond to the solvents listed in Table 2.

definite temperature. Thus, equilibrium 2 is displaced towards the cat-isomer at low temperatures, and towards the sq-isomer at high temperatures. It should also be noted that, at 260 K, in most cases, the dynamics of redox-isomerism is complicated by equilibrium 1, whose thermodynamic parameters are similar to the corresponding parameters of redox-isomerism. The data also show a significant solvent influence. Thus, for **3** when changing from hexane to CH_2Cl_2, $\Delta H°$ reduces from -2.9 kJ mol^{-1} to -13.0 kJ mol^{-1} with a simultaneous reduction in $\Delta S°$ from -34.7 J mol^{-1} K^{-1} to -56.1 J mol^{-1} K^{-1}.

Table 2

$\Delta H°$ (in kJ mol^{-1}) and $\Delta S°$ (in J mol^{-1} K^{-1}) values of the redox-isomerism equilibrium (eq. 2) for complexes **2** and **3**

Number [a]	Solvent	**2**		**3**	
		$\Delta H°$	$\Delta S°$	$\Delta H°$	$\Delta S°$
1.	2-Methylbutane	−2.1	−32.6	−6.7	−36.8
2.	Hexane	−2.9	−34.7	−7.1	−38.9
3.	Triethylamine, $AsEt_3$	−5.9	−43.1		
4.	Diethyl ether	−6.7	−44.8		
5.	Toluene	−5.4	−37.7	−10.0	−40.2
6.	Ethyl ethanoate	−7.5	−43.5		
7.	Tetrahydrofuran	−7.5	−44.4		
8.	Butan-2-one	−8.8	−46.4		
9.	Propanone	−9.6	−48.5		
10.	Chlorobenzene	−8.8	−45.2		
11.	Trichloromethane	−11.7	−55.6		
12.	Pyridine	−8.8	−42.7		
13.	Dichloromethane	−13.0	−56.1		

[a] The numbers correspond to the data in Fig. 1.

In moving from **2** to **1** (i.e. to a quinone of less acceptor ability) ΔH° increases from -13 kJ mol^{-1} to -3.3 kJ mol^{-1} (in CH_2Cl_2). In contrast, for complex **3**, containing a quinone of greater acceptor ability, the ΔH° value reduces from -7.1 kJ mol^{-1} (in hexane) as compared with -2.4 kJ mol^{-1} for **2**. Thus, the equilibrium position for the redox-isomerism is very sensitive to both changes in inner (the nature of the quinone ligand) and outer (the solvent) coordination spheres of a complex.

The kinetics of redox-isomerism

The rates of the forward and the reverse reactions of redox-isomerism are fast on the EPR time scale over the range 190 to 260 K. Such processes can be characterized by the EPR method if the contribution unsymmetrical broadening is known at the expense of exchange between the two paramagnetic forms to the overall width of the averaged EPR spectrum (the second term in eq. 6) [5].

$$W = W_0 + \gamma_e \tau P(1-P)\langle(\delta H_0)^2\rangle \tag{6}$$

In this case W is the overall width of the component m_i of the averaged EPR spectrum; W_0 is the line-width in the absence of this exchange; P and $(1-P)$ are mole fractions of cat- and sq-isomers, respectively; τ is the average lifetime of the isomers; γ_e is a gyromagnetic ratio for the electron; δH_0 is the distance between the corresponding components of the EPR spectra of cat- and sq-isomers.

The present work deals with the kinetics of redox-isomerism of complex **2** in hexane, toluene, diethyl ether and tetrahydrofuran. The τ value for a specified temperature has been determined by eq. 6, measuring the broadening of the components from $m_i = -\frac{3}{2}$ and $m_j = \frac{1}{2}$ of the observed EPR spectrum. The width of the component with $m_i = -\frac{1}{2}$ does not change during exchange since $\delta H_0 = 0$, and is therefore taken to be equal to W_0. To determine the rate constants, k_{sq} and k_{cat}, of both the forward and the reverse reactions of equilibrium 2, we used the relations 7–9.

$$K = \frac{k_{sq}}{k_{cat}} \tag{7}$$

$$\tau = \frac{\tau_{sq} \cdot \tau_{cat}}{\tau_{sq} + \tau_{cat}} \tag{8}$$

$$\tau = \frac{1}{k} \tag{9}$$

where τ_{sq} and τ_{cat} are the lifetimes of the sq- and cat-isomers, respectively. Based on the relationship of $\ln(k_{sq})$ and $\ln(k_{cat})$ with T^{-1}, the activation energies and pre-exponential factors of the forward and the reverse reactions (E_a^{sq} and A^{sq}; E_a^{cat} and A^{cat}, respectively) have been calculated by the least-squares method. Their values have been used to determine enthalpies ($\Delta H_{sq}^{\neq}$ and $\Delta H_{cat}^{\neq}$) and entropies ($\Delta S_{sq}^{\neq}$ and $\Delta S_{cat}^{\neq}$) of activation for the forward and the reverse reactions of the redox-isomerism equilibrium, according to equations 10 and 11.

$$E_a = \Delta H^{\neq} + RT_{av} \tag{10}$$

$$A = \frac{eKT_{av}}{h}\, e^{(\Delta S^{\neq}/R)} \tag{11}$$

The analysis of the kinetic data obtained allows some important conclusions to be drawn about the redox-isomerism equilibrium.

(a) When reaching the high temperature limit (ca. 280 K), the rates of the forward and the reverse reactions for the redox-isomerism equilibrium approach the rates of the progressively-rotating relaxation of dipoles in the liquid phase ($\omega_0 \approx 10^{11}$ s^{-1}), the latter controlling the reorganization of the solvent shell during the chemical reactions [6].

(b) $\Delta S^{\neq}_{sq}$ is negative in all solvents, and $\Delta S^{\neq}_{cat} \geqslant 0$. That is, the catecholate isomer is entropically less advantageous not only relative to the sq-isomer, but also relative to the activated complex.

The solvent role in the redox-isomerism equilibrium

The thermodynamic and kinetic parameters which have been obtained in the present work show that the solvent plays one of the key roles in the control of the redox-isomerism equilibrium at small values of ΔG. However, the solvent influence (Table 2) is not predictable: strongly coordinating solvents (e.g. pyridine, triethylarsine, triethylamine or thf) do not appear to influence the position of the redox-isomerism equilibrium to a greater extent than less polar solvents (e.g. hexane, toluene and CH_2Cl_2).

Additional arguments to confirm the absence of specific solvation have been gained from experiments with isomolal series of solvents. Solutions of complex **2** in mixtures of hexane/thf and hexane/$CHCl_3$ at different temperatures have been studied: a similar dependence of $A_i(^{75}As)$ upon solvent mole fraction was observed in both cases. At temperatures $> -50\,°C$, this dependence is practically linear. At temperatures $< -50\,°C$, in the region corresponding to a small mole fraction of the more polar solvent, there is positive deviation of the $A_i(^{75}As)$ values: with decreasing temperature, the deviation increases. Taken together, these factors point to the absence of strong ($> k_B T$) specific solvation interactions between solvent molecules and the metal complex.

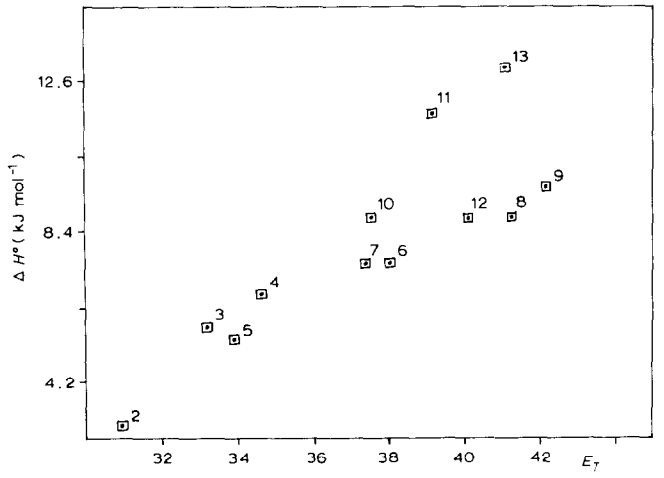

Fig. 4. Plot of $\Delta H°$ versus E_T for complex **2** in different solvents. The numbers correspond to the solvents listed in Table 2.

On the other hand, we cannot reveal good correlation of thermodynamic and kinetic parameters for the redox-isomerism equilibrium with parameters characterizing non-specific solvation of the solvents studied. Figure 4 shows ΔH° for the equilibrium 2 in different solvents according to the empirical parameter E_T. The latter [7] characterizes the polar and solvation properties of a solvent as a whole. Figure 4 demonstrates, that ΔH° values increase with increasing E_T, but there is no unique correlation between E_T and ΔH°.

In our view, the model accounting for solvent influence by means of the reorganization of the outer coordination sphere of the complex (consisting of solvent molecules) is the most appropriate to the experimental data obtained. In this model, a complex molecule is the organizing centre for an outer-sphere solvating shell, via different types of weak interactions with solvent molecules. In this case, the energy of interaction of the complex-solvating shell is similar to the value of $k_B T$ (the ΔG change range for the complex is $\leqslant 13$ kJ mol^{-1}; $k_B T$ for 200 K and 300 K is 1.7 and 2.5 kJ mol^{-1}, respectively). It is clear that, in the limits of this model, the complex for which $\Delta G \sim 0$ (not taking into consideration solvent influence) will be the most sensitive to solvent influence. In the compounds studied, **2** is such a complex: the complexes **1** and **4** lead to reduction of the ΔG_{sol} term contribution relative to the total energy of the redox-isomerism equilibrium. As a consequence, these last complexes are less sensitive to solvent influence.

In terms of this model, the deviation of $A_1(^{75}\text{As})$ dependence from linear in solvent mixtures at reduced temperatures may be explained in terms of increasing the specific solvent influence as $k_B T$ reduces.

On the strength of the data obtained, it is difficult to draw a conclusion about the nature of the complex-solvent interaction. It is likely to incorporate a whole spectrum of weak intermolecular interactions. The main factor defining the difference in solvation of the catecholate and semiquinone isomers is the different degree of charge separation in them (i.e. dipole moment). The catecholate isomer, containing rhodium with a formal oxidation state $+2$ as well as a formally dianionic ligand, has to have a higher degree of charge separation than its semiquinone isomer. On the one hand, the charge separation has to increase the dipole moment of the complex and hence the energy of its interaction with solvent molecules at the expense of electrostatic interactions. On the other hand, the charge increase leading to the relative excess of electronic density on the ligand and its concomitant deficit on the metal has to cause the intensification of donor–acceptor interaction with solvent molecules. Thus, catecholate isomers must "organize" their solvating shells more effectively the more polar the solvent. This shows itself in the ΔH increase with increasing solvent polarity. Simultaneously, ΔS reduces as the more "organized" solvating shell is more ordered.

The electronic and molecular structure of the redox-isomers

The redox-isomers studied here are not pure electronic isomers. Although their intertransformation is connected with intramolecular electron transfer, it has to be accompanied by a reorganization of the molecular structure. Due to the lability of the complexes studied (the majority of them are formed in solution only at temperatures < 280 K), we cannot directly determine their structure. However, based on the known data the coordition chemistry and the structure of d^7–d^8 pentacoordinate complexes of the platinum group metals, it is possible to make

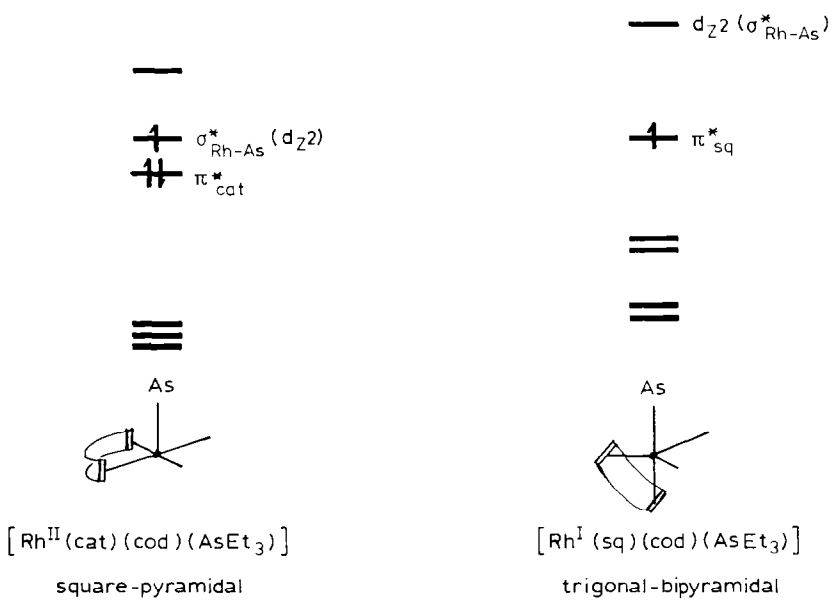

Fig. 5. The proposed geometry of the redox-isomers, and a diagram of their molecular orbitals.

some proposals about the molecular structure of the isomers. The most probable structure for sq-isomer is the trigonal bipyramid, in which the apical positions are occupied by $AsEt_3$ and one of the double bonds of cod (see Fig. 5). Such a structure is in good agreement with the EPR data and X-ray analysis data for isoelectronic and similar semiquinoneplatinum(II) complexes [8]. The cat-isomer, being a d^7-complex, most probably has a square pyramidal structure, also characteristic of π-complexes of the platinum group metals [9]. The possibility of the interconversion of these two structures is well established [10].

Arsine ligand addition to square-planar rhodium(I) proceeds at the expense of the antibonding arsine MO interaction with the d_{z^2} rhodium orbital. As a result of these interactions, two new MOs of the pentacoordinate complex form: bonding (σ_{Rh-As}) and antibonding ($\sigma^{\star}_{Rh-As}$) orbitals having the same symmetry as the d_{z^2} orbital. In this case, the energy of $\sigma^{\star}_{Rh-As}$-orbital is close in energy to the $\pi^{\star}_{sq}$ orbital (occupied by one electron in the initial square-planar complex). Thus, there are two orbitals close in energy but of different symmetry (and hence not interacting): the $\sigma^{\star}_{Rh-As}$ and $\pi^{\star}_{sq}$ orbitals are the highest-occupied ones in the pentacoordinate complex. The population of these two orbitals by three electrons, according to their relative energy, defines the geometry of the complex. When $E(\sigma^{\star}_{Rh-As}) > E(\pi^{\star}_{sq})$, two electrons are in the $\pi^{\star}_{sq}$-orbital (thus, in this case, the sq-ligand transforms into a catecholate ligand) and the unpaired electron occupies the $\sigma^{\star}_{Rh-As}$ orbital. Hence the complex represents itself as a catecholate rhodium(II) complex with square pyramidal geometry. The Rh–As bond in this complex is partially destabilized by the one unpaired electron in the antibonding $\sigma^{\star}_{Rh-As}$ orbital.

In the case where $E(\sigma^{\star}_{Rh-As}) < E(\pi^{\star}_{sq})$, two electrons must be placed in the $\sigma^{\star}_{Rh-As}$ orbital, which would correspond to a semiquinonerhodium(I) complex with square-pyramidal geometry. However, in this case, the filling of the antibonding

Table 3

Values of $\Delta H^{\neq}_{sq}$, $\Delta S^{\neq}_{sq}$, $\Delta H^{\neq}_{cat}$ and $\Delta S^{\neq}_{cat}$ for the redox-isomerism equilibrium for the complex 2

Solvent	sq → cat		cat → sq	
	$\Delta H^{\neq}$ (kJ mol^{-1})	$\Delta S^{\neq}$ (J mol^{-1} K^{-1})	$\Delta H^{\neq}$ (kJ mol^{-1})	$\Delta S^{\neq}$ (J mol^{-1} K^{-1})
Hexane	8.4	−34.7	11.3	−0.4
Tetrahydrofuran	7.5	−38.5	16.3	11.7
Diethyl ether	8.4	−31.4	14.6	12.1
Toluene	11.3	−25.1	15.9	9.6

$\sigma^{\star}_{Rh-As}$ orbital with two electrons completely destabilizes the Rh–As bond in the complex and the existence of semiquinonerhodium(I) complexes with square-pyramidal geometry becomes impossible. In the alternative coordination geometry (trigonal bipyramidal) the MO order is such that the orbital (arising from d_{z^2}) responsible for the Rh–As antibonding appears as the highest in energy, and that is why the unpaired electron occupies the $\pi^{\star}_{sq}$ orbital and one of the two orbitals (d_{xy} or $d_{x^2-y^2}$) is the highest fully-occupied MO, which leads to the partial rhodium antibonding with equatorial ligands (as was established for the isoelectronic semiquinoneplatinum(II) complexes with such geometry).

In summary, it may be said that the existence of two redox-isomers rapidly interconverting with intramolecular metal–ligand electron transfer is not well described in the literature, in contrast to the well-known processes of metal–ligand electron transfer in complexes of the Creutz–Taube type [11] and of the ligand–ligand ("wandering valency") type [12]. This widening of the field provides special interest, especially in connection with possible uses as functional models for intramolecular electron transfer in such biochemical processes as photosynthesis [13] and breathing [14], which are extraordinarily sensitive to outer-sphere parameters.

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