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A. Fantola Lazzarini, E. Lazzarini, M. Mariani. Further results on the relationship between the rate constants of o-Ps into p-Ps conversion and the electron delocalization in 3d complexes. Journal de Physique IV Proceedings, 1993, 03 (C4), pp.C4-113-C4-119. 10.1051/jp4:1993413 . jpa-00251456

HAL Id: jpa-00251456

<https://hal.science/jpa-00251456>

Submitted on 1 Jan 1993

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Further results on the relationship between the rate constants of o-Ps into p-Ps conversion and the electron delocalization in 3d complexes

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SUMMARY

The ortho into para-positronium conversion reactions promoted by the paramagnetic complexes formed with ethylenediaminetetraacetic acid (H_4EDTA) by Mn(II), Fe(II), Co(II), Ni(II) ions were studied at various temperatures. The results are discussed together with those previously obtained for the Cr(III) and Cu(II) complexes with the same ligand. It was found that the rate constants, k_{SE} , are larger for complexes: A) whose 3d inter-electronic repulsion parameter attains smaller values; and B) for which spin orbit coupling occurs. These findings give further support to our proposal that the o-Ps into p-Ps conversion reaction may be used to investigate the electron delocalization in paramagnetic 3d complexes.

INTRODUCTION

Ps atoms may undergo several types of chemical reaction, among them the conversion reaction (SE), which consists of o-Ps being converted into p-Ps atoms (and vice versa) by interacting with paramagnetic species.

Recently, we have found that the rate constants k_{SE} of o-Ps into p-Ps conversion reactions promoted by Fe_{aq}^{2+} ; Co_{aq}^{2+} ; Ni_{aq}^{2+} and Cu_{aq}^{2+} aqua-ions are twice as large as those of the Cr_{aq}^{3+} and Mn_{aq}^{2+} ions (~ 2.0 against $\sim 1 M^{-1}ns^{-1}$)¹. It should be noted that the magnetic moments μ_{eff} of the first four ions are of the SOC type (SOC = spin orbit coupling), while those of Cr_{aq}^{3+} and Mn_{aq}^{2+} are of the spin only (SO) type.

The explanation advanced is based on the fact that the k_{SE} values of the o-Ps to p-Ps conversion reactions promoted by 4f, 3d aqua ions

and the ammoniated electron increase in the order $k_{SE}(4f)^2 \ll k_{SE}(3d) \ll k_{SE}(e_{am}^-)^3$, ($0.05 : \text{ca. } 2 : 50 \text{ M}^{-1}\text{ns}^{-1}$). That is, k_{SE} s seem to increase as the spin density of the unpaired electrons increases at the collision site between the ion and Ps atom. Consequently, it was argued that the delocalization of the unpaired metal electron (and consequently the k_{SE}) should be larger when SOC occurs. Details may be found in ref.1.

Subsequently, a systematic investigation carried out on 14 Cr(III) complexes, has ascertained that the k_{SE} s are also correlated with the corresponding β ratios between the inter-electronic repulsion parameter of the complex, B , and that of the free gaseous ion, B_0^4 . We recall that the β values are less than 1 and different for the various complexes. This means that the 3d inter-electronic repulsion is less in complexes than in the free gaseous ion due to the expansion of the 3d electron cloud of the metal ion towards the ligand donor⁵. The experimental results show indeed that k_{SE} increases as the β value decreases.

Continuing our work, the k_{SE} s of the Mn(II); Fe(II); Co(II) and Ni(II) complexes with the ethylenediaminetetraacetic acid ($H_4\text{EDTA}$) ligand were measured. The results are here described and discussed with those of the same Cr(III)⁴ and Cu(II)⁶ complexes already measured.

The measurements were made at different temperatures in order to ascertain whether the reactions were diffusion controlled (DCR) as are those occurring between Ps and the Cr(III) and Cu(II) complexes already investigated.

EXPERIMENTAL

Materials.— The complexes were prepared according to the literature^{7,8}. Their formulae in aqueous solutions are $[M^{II}(\text{EDTA})H_2O]^{2-}$, but while the EDTA^{4-} ion behaves as a pentadentate ligand for Fe(II), Co(II), Ni(II), Cr(II) and Cu(II), by contrast it is hexadentate in Mn(II) complex, which therefore is a heptacoordinate⁹. The rate constants were derived from PAL (Positron Annihilation Lifetime) spectroscopy. A conventional fast-fast coincidence system already described was used¹. The PAL spectra were decomposed into three components by using the POSITRONFIT program¹⁰; no constraint for the component intensities and lifetimes was imposed.

The rate constants of o-Ps into p-Ps conversion were calculated by

means of Eqn(1) which relates the decay constant, λ , of the long lived component of the PAL spectra to the decay constant $\gamma = k_{SE} c$ of the o-Ps into p-Ps conversion reaction, c being the solute concentration:

$$\lambda = 2\gamma + \frac{\lambda_s + \lambda_t}{2} + \lambda_{PO} - \left[3\gamma^2 + \left(\gamma + \frac{\lambda_s - \lambda_t}{2} \right)^2 \right]^{1/2} \quad (1)$$

λ_s and λ_t are the p-Ps and o-Ps intrinsic decay constants in aqueous solution (6.4 and 0.0057 ns^{-1})¹, and λ_{PO} is the decay constant by pick off, also in aqueous solution. It was assumed that λ_{PO} is independent of c and equal for both o-Ps and p-Ps atoms. In pure water its value is $0.540 \pm 0.005 \text{ ns}^{-1}$.

γ values, deduced from the λ values (eqn.(1)), were normalized to the pure H_2O viscosity by multiplying them by the $\eta(c)/\eta(\text{H}_2\text{O})$ ratio¹ where $\eta(\text{H}_2\text{O})$ is the viscosity coefficient of pure water and $\eta(c)$ that of the solution at concentration c . Finally, k_{SE} was deduced from the slope of the straight line interpolating the γ values vs. c .

Assignment of Reaction Type.— The reactions of o-Ps atoms with our H_4EDTA complexes are of the SE type, as it was ascertained by means of the Doppler Broadening of Annihilation Radiation (DBAR) spectra. These experiments were carried out at room temperature ($22 \pm 1^\circ\text{C}$).

Our DBAR spectrometer was equipped with a planar HPGe detector ($200 \text{ mm}^2 \times 10 \text{ mm}$) supplied by ORTEC. The FWHM (Full Width at Half Maximum), ΔW_γ , for the 496 keV γ ray emitted in the ^{103}Ru decay is 0.94 keV , while that of the overall annihilation peak ΔW_{An} in pure water is 2.52 keV .

The AR curves were decomposed into four Gaussian components by using the ACARFIT program¹¹ and applying as constraints the FWHMs, ΔW_i , of the various annihilation modes. We recall here that while the ratio between o-Ps and p-Ps formation probabilities P_{o-Ps}/P_{p-Ps} is 3, that between the corresponding intensities I_{o-Ps} and I_{p-Ps} of annihilation radiation is 3.3 due to p-Ps annihilations by pick off.

The $I_{p-Ps}(c)$ in converter solution at concentration c is given by eqn.(2):

$$\frac{I_{p-Ps}(c)}{P_{p-Ps}(0)} = \left[\frac{\lambda_s (\lambda_t + \lambda_{PO} + 4k_{SE}c)}{k_{SE}c(\lambda_s + 3\lambda_t + 4\lambda_{PO}) + (\lambda_t + \lambda_{PO})(\lambda_s + \lambda_{PO})} \right] \quad (2)$$

where P_{p-Ps} , $\lambda_{s,t}$, λ_{PO} , k_{SE} have been already defined.

Solutes may also cause inhibition of Ps formation. Several equations have been suggested for relating $I_{Ps}(c)$ to the solute concentration^{12,13,14}. In many cases the following empirical equation may be safely used up to $c=1-1.5M$:

$$P_{Ps}(c)/P_{Ps}(0) = (1-f) + f/(1-Kc) \quad (3)$$

where K (in M^{-1}) is the inhibition constant dependent on the solute type and f is the maximum inhibition fraction, also dependent on solute and solvent.

Consequently, if the paramagnetic species also promotes inhibition of Ps formation, the right side of Eqn.(2) should be multiplied by the right side of Eqn(3).

RESULTS

In order to ascertain whether the reactions were DC, the k_{SE} values of each complex were analyzed according to a procedure already described¹. It was found that this is so. For the sake of conciseness we given here only the k_{SE}^{298} s at 298 K (Table 1).

TABLE 1

The k_{SE} in $M^{-1}ns^{-1}$ at 298 K of *o*-Ps into *p*-Ps conversion reactions promoted by aqua and H_4EDTA complexes of named metal ions are shown. Their β values are also given when available. Even if unknown, the β values of H_4EDTA complexes are larger than those of the corresponding aqua ions. The type of magnetic moment is also mentioned. (details in the text).

Ion	k_{SE} of aqua ions ref.1	β ref.15	Spin orbit coupling?	k_{SE} of H_4EDTA complexes	β ref.15	Spin orbit coupling?
Cr(III)	1.01±0.09	0.79	No	1.42±0.02	0.75	No
Mn(II)	1.01±0.06	0.930	No	1.06±0.03	0.916	No
Fe(II)	2.26±0.02	—	Yes	3.01±0.06	—	Yes
Co(II)	2.16±0.12	0.76	Yes	2.41±0.05	0.71	Yes
Ni(II)	2.58±0.03	0.88	Yes	3.15±0.15	0.85	Yes
Cu(II)	~1.6	—	Yes	~ 2.4	—	Yes

The results of DBAR measurements may be summarized as follows. The AR peaks of all complexes may be decomposed into four components, which were ascribed to p-Ps, o-Ps, free e^+ and annihilations in the source mounting (4%).

The variances of the final fits ranged between 0.85-1.20 for 65-70 degrees of freedom and the experimental and back-calculated ΔW_{An} values agreed within experimental error (± 0.02 keV).

FIG.1 - The points are the experimental $I_{p-Ps}(c)$ values of $[Ni(EDTA)H_2O]^{2-}$ complex. Curve B is the plot of the theoretical intensity, I_T , vs. c (Eqn.2) at 22.5°C ($k_{SE} = 3.1 \text{ M}^{-1}\text{ns}^{-1}$) assuming that Ps inhibition does not occur, while curve A takes into account inhibition of Ps formation (Eqn.3 with $f = 0$ and $K = 0.37 \pm 0.02$). The plot of Eqn.3 from which the f and K values were deduced, is shown in the insert.

The experimental trend of I_{p-Ps} vs. c is similar for all the complexes investigated, (see e.g. fig.1, curve A). The expected trend of $I_T(c)$ calculated at 22.5°C with Eqn.(2) is given by the curve B of the same figure, that is in all cases the calculated intensities $I_T(c)$ were found to be bigger than the experimental ones. Thus it was hypothesized that the complexes are also inhibitors of Ps formation. The inhibition constants K were obtained by means of eqn(3).

It was found that the complexes investigated are total inhibitors of Ps formation and that their inhibition constants are as follows:

$$\begin{array}{ll} K[Mn(II)] = 0.11 \pm 0.01 & K[Fe(II)] = 0.21 \pm 0.02 \\ K[Co(II)] = 0.12 \pm 0.01 & K[Ni(II)] = 0.37 \pm 0.02 \end{array}$$

The extrapolation of the experimental $I_{p-Ps}(c)$ values vs. c obtained by inserting Eqn.(3) in Eqn.(2) and by using the k_{SE} and K values given above is rather good (curve A of Fig. 1).

Finally it may be concluded that:

- A) the four reactions investigated are DCRs as those promoted by the two complexes $[Cr(EDTA)H_2O]^-$ and $[Cu(EDTA)H_2O]^{2-}$ previously studied;
- B) the complexes studied promote the o-Ps into p-Ps conversion reaction and inhibition of Ps formation.

In order to simplify the following discussion the k_{SE} of the aqua-ions were also collected in Table 1.

DISCUSSION

The main conclusions reached may be summarized as follows:

- A) the trend of the k_{SE}^{298} of the H_4EDTA complexes parallels that of the k_{SE}^{298} of the aqua-ions. That is, the k_{SE}^{298} of complexes, whose μ_{eff} is of SO type, are smaller than those of the complexes for which μ_{eff} is of the SOC type;
- B) the k_{SE}^{298} values of the H_4EDTA complexes are generally larger than those of the corresponding aqua-ions. In fact the β values of aqua ions are larger than those of the H_4EDTA complexes. The rather similar k_{SE}^{298} values of the two $Mn(II)$ complexes may, indeed, be justified by the fact that the β values of $Mn(II)$ complexes are very similar to each other¹⁵. Moreover, it cannot be disregarded that while Mn_{aq}^{2+} ion is hexacoordinate, the $[Mn(EDTA)H_2O]^{2-}$ complexes is heptacoordinated. This causes an increase of the bond lengths with a consequent possible increase of the β value of the $EDTA^{4-}$ complex with respect to that of Mn_{aq}^{2+} . On the contrary, we

have no sure explanation at the moment for the small difference between $k_{SE}[(\text{CoEDTA})^{2-}]$ and $k_{SE}[\text{Co}_{aq}^{2+}]$.

In conclusion the first statement confirms the role of SOC in delocalization of the unpaired metal electrons and the second supports, or at least does not contradict, the statement that k_{SE} increases as the 3d electron cloud expands towards the donor atoms and the complex periphery.

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