ELECTRONIC CONSTITUTION OF PARAMAGNETIC 3d COMPLEXES AND POSITRONIUM CONVERSION RATE CONSTANTS

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The rate constants, k_{SE}, of *ortho-* into *para*-positronium spin conversion reactions promoted by paramagnetic 3d complexes may be correlated with their electronic constitution as it is described by the spin–orbit coupling and interelectronic repulsion parameters. The correlation is explained in terms of unpaired metal–electron delocalization towards the complex boundaries.

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1. Introduction

Ortho-positronium may be converted into *para*-positronium (and vice versa) by interacting with paramagnetic compounds such as solvated electron 3d and 4f complexes, etc. The rate constants of *ortho-* into *para*-Ps conversion reactions, k_{SE}, depend on the particular paramagnetic compound considered, e.g. the k_{SE}'s of ammoniated electron (e_{am}^-), 3d and 4f aquo-ions are in the ratio 10:1:0.01 [1, 2]. This finding suggested that the k_{SE}'s may depend on the spin density of unpaired electrons at the collision site between Ps and paramagnetic compound.

In order to support the hypothesis, a systematic investigation was carried out, in particular, the k_{SE} of the aquo-ion Cr(III) complexes listed in Table I and III were checked or measured for the first time.

2. Experimental

2.1. Chemicals

A few compounds were purchased, but the great part of them were prepared according to literature.

2.2. Reaction type

As chemical entities, Ps atoms may promote several types of reactions, among them the spin-exchange (SE) and oxidation (Ox) reactions. It was ascertained by means of ACAR (Angular Correlation of Annihilation Radiation) or DBAR (Doppler Broadening of Annihilation Radiation) measurements that all the compounds studied promote only the o-Ps into p-Ps conversion reactions (henceforth simply called "conversion reactions"), but Cu_{aq}^{2+} which may promote both SE and Ox reactions. Then its ACAR curves were analysed in order to obtain the k_{SE} and k_{Ox} contributions to the overall rate constant as described in Ref. [3]. The Cu_{aq}^{2+} rate constant as shown in Table I is the k_{SE}.

2.3. Positron source

About 0.5 MBq ($\approx 15 \mu Ci$) of ^{22}Na from a carrier-free neutral solution supplied by Amersham were deposited between two identical kapton foils (1.065 mg cm^{-2}) which were sealed together with a cyanoacrilate adhesive. The source was suspended in vials containing the reactant solution. O_2 was removed from the vials by bubbling N_2. During the measurements the temperature was kept constant within 0.1 K.

2.4. Annihilation spectra

Apparatuses and methods have been already described [4]. Shortly, the k_{SE} values were obtained from the decay constant λ of the component of the time spectra with the longest meanlife as described in Refs. [2, 4].

2.5. Kinetics of the SE conversion reactions

The k_{SE} were measured at different temperatures and the results were analysed as described in Ref. [4] to ascertain whether the reactions were diffusion controlled. Since this was confirmed and the rate constants of diffusion controlled reactions depend on the viscosity coefficient of the reaction medium and therefore on the reactant concentrations, λ and therefore k_{SE} values are normalised to the viscosity coefficient of pure water as described in Ref. [2]. The viscosity coefficients of the reaction media were measured by means of a KPG Ubbelohde Viscosimeter (B.S. 188; ASTM 2515; Jenaer Glasswerk Schott and Gen; Mainz).

3. Results

Only the rate constants at 298 K are reported here, since they are enough for supporting our working hypothesis. The data concerning the aquo-ions are shown in Table I from which it may be noted: (a) that the k_{SE}'s do not depend on the unpaired electron number, i.e. on the spin-only magnetic moment, μ_{SO}; and (b) that on the bases of the k_{SE} values the ions may be divided into two groups, the k_{SE}'s of the first group, formed by Mn_{aq}^{2+} and Cr_{aq}^{3+} ions, are $\approx 1 M^{-1} ns^{-1}$, whereas those of the second group, formed by Fe_{aq}^{2+}, Co_{aq}^{2+}, Ni_{aq}^{2+}, and Cu_{aq}^{2+} ions are about

TABLE I
k_{SE} [$M^{-1}ns^{-1}$] of listed aquo-ions. Spin-only, μ_{SO}, and experimental, μ_{eff}, magnetic moments in Bohr's magneton [BM] are also shown (μ_{eff} and μ_{SO} from Ref. [5]).

| Ion	Cr^{3+}_{aq}	Mn^{2+}_{aq}	Fe^{2+}_{aq}	Co^{2+}_{aq}	Ni^{2+}_{aq}	Cu^{2+}_{aq}
k_{SE}	1.01 ± 0.9	1.09 ± 0.05	2.26 ± 0.02	2.21 ± 0.07	2.58 ± 0.03	≈ 1.6
μ_{SO}	3.87	5.92	4.90	3.87	2.83	1.73
μ_{eff}	3.8	5.9	5.3	5.1	3.2	1.9–2.0

twice bigger. Looking for an explanation one may observe that only for the ions of the second group μ_{eff} is bigger than μ_{SO}, i.e. spin–orbit coupling occurs only for the ions of the second group. This trend can be easily justified if one supposes that k_{SE} increases as the density of unpaired metal electrons increases at the collision site between complex and Ps atom (i.e. at the complex boundaries and that the electron delocalization from atom is larger when spin–orbit coupling occurs. Measurements in progress suggest that the same conclusion is also true for the complexes formed by the same metal ions with H_4EDTA (ethylenediaminetetraacetic acid).

TABLE II
β ratios of Cr(III) complexes formed with sets of six equal mono- or three equal bidentate ligands. The nephelauxetic effect increases as β decreases [8] (ox^{2-} = oxalate, en = ethylenediamine).

Ligand	$6H_2O$	6urea	$6NH_3$	$3ox^{2-}$	3en	$6NCS^-$	$6CN^-$	$6Cl^-$
β	0.79	0.72	0.71	0.68	0.67	0.62	0.58	0.56

In order to discuss the data of Table II some basic chemistry must be recalled [6]. The fivefold degenerate $3d$ orbitals of Cr(III) gaseous ion in an octahedral arrow of six equal ligands (e.g. six CNS^- or CN^- ions or six H_2O or NH_3 molecules) are split into a lower triplet, t_{2g}, and an upper doublet, e_g, the separation between them, usually called $10\,Dq$, depends on the ligands which may be arranged in a series of increasing capability to cause $3d$ orbital splitting [6]. The series is in part

$$6Cl^- < 3C_2O_4^{2-} \text{ (or } 3ox^{2-})$$

$$\approx 6H_2O < 6NCS^- < 6NH_3 < 3(CH_2NH_2)_2 < 6CN^-.$$
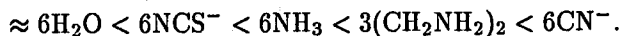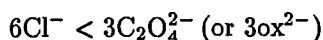
Since absorption transitions may occur between triplet and doublet states, the $10\,Dq$ separation value can be measured by UV absorption spectroscopy. For octahedral Cr(III) complexes the absorption spectra consist of three transitions whose energies $\bar{\nu}$ [cm^{-1}] are given by Eqs. (1a) and (1b) [7]:

$$\bar{\nu}_1 = 10\,Dq \tag{1a}$$

$$\bar{\nu}_{2,3} = 7.5B + 15\,Dq \pm 0.5\left\{225B^2 + 100\,(Dq)^2 - 180B\,Dq\right\}^{1/2}, \tag{1b}$$

where B is the Racah interelectronic repulsion parameter. The B values of complexes are smaller than the B_0 value of the free gaseous ion (i.e. $B/B_0 = \beta < 1$), this means that the overlapping of metal and ligand orbitals provides a path by which metal electrons can, and do, escape to a certain extent from $3d$-ion towards ligands and molecule boundaries. The effect has been named "nephelauxetic" (expanding cloud, from Greek) [6]. Summing up: β values, which can be derived by means of spectrochemical measurements, decrease as the electron delocalization from metal atom towards ligands increases.

The ligands can be arranged in a series of increasing capability to cause d cloud expansion, that is, of decreasing β values [8]. The series for Cr(III) is shown in part in Table II. For complexes formed with sets of mixed ligands an "average environment rule" [9] applies, i.e. the β value of these complexes are given by Eq. (2):

$$\beta = 1 - h\sum n_i\beta_i/r_J, \tag{2}$$

where β_i is the B/B_0 ratio for a set of six equal mono- or three equal bidentate ligands; n_i is the number of i-th ligand in the complex; r_J is 6 for mono- and 3 for bidentate ligands; h depends on $3d$ ion, in particular for Cr(III) it is $h = 0.21$.

Since the rate constants k_{SE} of o-Ps to p-Ps conversion reactions should increase as the spin density of unpaired electrons at complex boundaries increases, we argued that the k_{SE} and β values of Cr(III) complexes should be correlated.
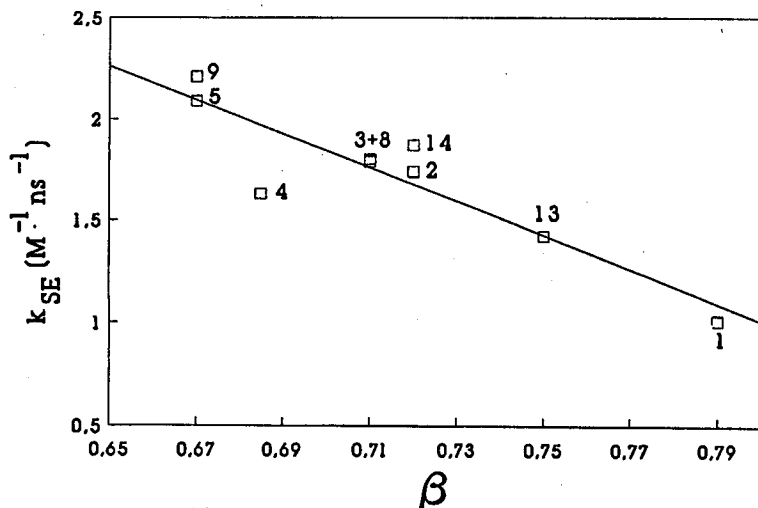

Fig. 1. The k_{SE} values of complexes 1–5 and 8–11 of Table III plotted against their β values. See Table III for point numeration.

Actually the data of Table III suggest that k_{SE} increases as β ratio decreases (items 1–7). The hypothesised relationship emerges, perhaps more clearly,

k_{SE} (M^{-1} ns^{-1}) at 298 K of the o-Ps to p-Ps SE reactions promoted by the following Cr(III) complexes. $\bar{k}_{SE}$ are the backcalculated rate constants using the "average environmental rule" (see the text).

Item[•]	Complex	k_{SE}	β	$\bar{k}_{SE}$	$100\frac{k_{SE}-\bar{k}_{SE}}{k_{SE}}$
1	Cr^{3+}_{aq} K-alum	1.01 ± 0.09	0.79^*	0.99	+2
2	$[Cr(urea)_6]Cl_3$	1.74 ± 0.06	0.72^*	1.74	ns^o
3	$[Cr(NH_3)_6]Cl_3$	1.79 ± 0.03	0.71^*	1.80	–
4	$K_3[Cr\ ox_3]$	1.63 ± 0.09	0.68^*	1.83	−12
5	$[Cr\ en_3]Cl_3$	2.09 ± 0.06	0.67^*	2.19	−5
6	$K_3[Cr(CNS)_6]$	8.15 ± 0.17	0.62^*	7.97	+2
7	$K_3[Cr(CN)_6]$	6.85 ± 0.12	0.58^*	6.85	ns^o
8	$[Cren_2(H_2O)_2]_2(S_2O_3)_3$	1.80 ± 0.03	$0.71^\triangle$	1.79	–
9	$[Cren_2ox]Cl$	2.21 ± 0.07	$0.67^\triangle$	2.07	+6
10	$[Cren_2(CNS)_2]CNS$	4.96 ± 0.13	$0.65^\triangle$	4.12	+17
11	$[Cr(H_2O)_5Cl]Cl_2$	2.63 ± 0.15	$0.75^\triangle$	2.64	–
12	$NH_4[Cr(NH_3)_2(CNS)_4]$	5.07 ± 0.18	$0.75^\triangle$	5.94	−17
13	$K[CrEDTA\ H_2O]$	1.42 ± 0.02	0.75	1.39	+2
14	$[Cr(NH_3)_5H_2O](NO_3)$	1.87 ± 0.03	$0.72^\triangle$	1.66	+11

[•] ox^{2-} = oxalate, $H_4(EDTA)$ = ethylenediaminetetraacetic acid, en = ethylenediamine.

[*] Experimental results,

[$\triangle$] Calculated by means of the "average environment rule" (Eq. (2)).

[o] Not significant, since the ligands appear in only one complex.

by plotting the k_{SE}'s of the following three series of complexes vs. their β values: $[Cr(NH_3)_{6-n}(CNS)_n]^{+(3-n)}$ ($n = 0, 4, 6$); $[Cren_{3-n}(CNS)_{2n}]^{+(3-n)}$ ($n = 0, 1, 3$); $[Cren_n(H_2O)_{6-2n}]^{3+}$ ($n = 0, 1, 2, 3$) ($[CrEDTA]^-$ was considered equivalent to $[Cren(H_2O)_4]$). Indeed, the k_{SE} values of each series are linearly dependent on n and therefore on β.

Thus an "average environment rule", similar to that valid for β ratios, should also be valid for k_{SE} values. According to this hypothesis and by applying the method of maximum likelihood to the k_{SE}'s of Table III, the contribution of each ligand used was deduced. The backcalculated $\bar{k}_{SE}$ values are also shown in Table III. The agreement between k_{SE} and $\bar{k}_{SE}$ values is rather satisfactory.

Finally the k_{SE}'s may also depend on other parameters which can cause electron delocalization, e.g. π bonding (as for Cl^- and CN^- ligands) or appropriate resonant structures (as for NCS^-). When such factors do not play a role, the k_{SE} are linearly dependent on β as can be verified by plotting the data of complexes 1–5 and 8–11 of Table III against the corresponding β values (Fig. 1).

Thus one may wonder whether the time is ripe for Ps to be used as a probe for studying the chemical constitution of complexes.

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