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Lifetimes of *ortho*-Positronium in Benzene Solutions of β-Diketonates of Iron(III) and Cobalt(III)

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The lifetimes of *ortho*-positronium (*o*-Ps) have been measured in benzene solutions of β-diketonates of iron(III) and cobalt(III). A trend in substituent effect on the acceleration of *o*-Ps decay has been found. A substituent such as trifluoromethyl, that tends to withdraw electrons from the chelate ring, greatly accelerated *o*-Ps decay; the greatest rate constant observed was $33.8\times10^9\ M^{-1}\ s^{-1}$ for tris(hexafluoroacetylacetonato)iron(III). An electron-releasing substituent such as *t*-butyl accelerated *o*-Ps decay to a lesser extent, *e.g.* $10.5\times10^9\ M^{-1}\ s^{-1}$ for tris(dipivaloylmethanato)iron(III). The extent to which a complex accelerated *o*-Ps decay was largely related to the redox potential, which was observed by cyclic voltammetry. Complexes with phenyl substituents in the ligand showed slightly smaller effects than that suggested by their redox potentials.

Chemical reactions of *ortho*-positronium (*o*-Ps) in aqueous solutions have been investigated by many workers,1—9) who have shown that the reactions of *o*-Ps with solute species can be characterized essentially as one or the other type: oxidation of *o*-Ps, and spin-conversion of *o*-Ps to *para*-positronium (*p*-Ps) and *vice versa*. Highly oxidizing ions such as MnO_4^- and CrO_4^{2-} oxidized *o*-Ps, resulting in a decrease in the lifetime and intensity of *o*-Ps.2,3) Bartal and Ache7) reported that the reactions of *o*-Ps show some similarities to those of the hydrogen atom in aqueous solutions of Werner-type cobalt(III) complexes. In nonaqueous systems, however, the interaction of *o*-Ps has not been systematically investigated. In nonaqueous solvents such as benzene, positrons and positronium as well as solute species are solvated to a lesser extent than in aqueous solutions. There is no evidence to prove whether positrons and positronium in benzene are solvated or not, but molecular orbital calculations have shown that the positron is barely bound to benzene.10,11) Thus *o*-Ps will react with solute species in a way more characteristic of dissolved species. In a previous paper,12) it was shown that *o*-Ps is oxidized by acetylacetonates and dipivaloylmethanates of iron(III) and manganese(III), and that the decay rate constant strongly depends on the redox potential of the solute. The reaction of *o*-Ps with solutes may however be influenced by the outer constituent of the solute molecule and the reaction mechanism may not be so simple. Thus, it is of interest to study the reaction of *o*-Ps with a series of complexes which are identical in the first coordination sphere but differ in the periphery.

A series of β-diketones form chelates of similar structure with a variety of metal ions. Among them, iron(III) forms tris chelates of high-spin ($S=5/2$) type, while cobalt(III) forms chelates of low-spin ($S=0$) type. In the present study, the lifetimes of positrons and positronium decaying in benzene solutions of β-diketonates of iron(III) and cobalt(III) have been measured. These complexes have different electronic densities at the metal center with different substituents in the ligands, thus showing different redox potentials. Another type of acceleration of *o*-Ps decay, due to spin-conversion mechanism, may occur in the presence of unpaired electrons. A comparison of the reaction rates for diamagnetic cobalt(III) and paramagnetic iron(III) complexes will enable the mechanism of *o*-Ps decay to be elucidated.

Experimental

Preparation of β-Diketonates. The following chemicals of reagent grade were used for the preparation of iron and cobalt complexes without further purification: acetylacetone (Hacac), dipivaloylmethane (Hdpm), trifluoroacetylacetone (Htfa), hexafluoroacetylacetone (Hhfa), 2-thenoyltrifluoroacetone (Htta), benzoyltrifluoroacetone (Hbta), dibenzoylmethane (Hdbm), benzoylacetone (Hbza), and 3-phenylacetylacetone (Hpaa).

Tris(β-diketonato)iron(III) complexes were prepared by the reaction of iron(III) sulfate or nitrate with the corresponding β-diketones.13,14) $Fe(hfa)_3$, $Fe(tfa)_3$, $Fe(acac)_3$, and $Fe(dpm)_3$ were purified by repeated vacuum sublimations. $Fe(tta)_3$, $Fe(dbm)_3$, $Fe(bta)_3$, $Fe(bza)_3$, and $Fe(paa)_3$ were recrystallized from a benzene–hexane mixture. The preparation of aluminium complexes was essentially the same as that for the corresponding iron compounds. $Co(acac)_3$ was synthesized by the method of Moeller,13) and $Fe(dpm)_3$ by Hammond *et al.*14) $Co(tfa)_3$ and $Co(bza)_3$ were prepared from $Na_3[Co(CO_3)_3]3H_2O$, and purified on an alumina column.15)

Lifetime Measurements. A specified amount of each complex was dissolved in benzene, and the solution was kept in a Pyrex-glass tube which contained a positron source of nearly 6 μCi of $^{22}Na(NaCl)$ of high specific activity. The $^{22}Na(NaCl)$ was sealed with aluminium foil, such that annihilation of positrons in the foil was negligibly small. The sample solution was degassed by repeated vacuum freeze-thaw treatments. The lifetime of positrons and positronium was measured with a fast-slow coincidence system constructed by the authors, the details of which were reported elsewhere.16) The time resolution of the system was determined to be 750 ps (full width at half maximum) with prompt γ-rays of ^{60}Co under the same condition as that for positron measurements. The lifetime of *o*-Ps was obtained from the slope in the lifetime spectrum.

Cyclic Voltammetry. Cyclic-voltammetric measurements were made on β-diketonates of iron(III) and cobalt(III) in *N*,*N*-dimethylformamide (DMF), using 0.1 M tetrabutylammonium perchlorate (TBAP) as the supporting electrolyte. The measurement was conducted in a three-necked cell at room temperature. A platinum inlay electrode (Beckman 32273) was used as the working electrode; the counter electrode was a piece of platinum wire. A saturated Ag/AgCl electrode as reference was connected to the cell by the two salt bridges: saturated KCl in water, and 0.1 M TBAP in DMF. A Hokuto Denko Model HA-101 potentiostat and a Hokuto Denko Model HB-107 function generator were used. Voltammograms were recorded on a Rikadenki X-Y recorder Model BW-133.

Results and Discussion

Benzene–Acetylacetone System. The lifetime spectra of positrons and positronium were measured in mixture of benzene and acetylacetone (Hacac). The lifetime (τ_2) of *o*-Ps in the mixture was essentially the same irrespective of the molar fraction of acetylacetone, whereas the *o*-Ps intensity (I_2) decreased with increasing molar fraction of Hacac (from 34.4% for pure benzene to 10.4% for pure acetylacetone), as shown in Fig. 1. The ionization and UV spectroscopy data suggest that no remarkable difference in the Oré gap model exists between benzene and acetylacetone, and thus the observed trend in I_2 values is not explainable by a simple Oré model.

Assuming the compounds of the mixture behave additively in the formation of *o*-Ps, the I_2 value for a mixture containing acetylacetone at a molar fraction of x may be expressed by

$$I_2 = \frac{\lambda_{pb}(1-x)+\lambda_{pa}x}{(\lambda_{pb}+\lambda_{qb})(1-x)+(\lambda_{pa}+\lambda_{qa})x}, \qquad (1)$$

where λ_{pb} and λ_{qb} are respectively the average rate of *o*-Ps formation and that of annihilation without forming *o*-Ps in pure benzene, and λ_{pa} and λ_{qa} are those in pure acetylacetone. The curve in Fig. 1 shows the I_2 values calculated from Eq. 1, assuming $\lambda_{qb}/\lambda_{pb}=2$, $\lambda_{pa}/\lambda_{pb}=4$, and $\lambda_{qa}/\lambda_{pb}=34$. Within the experimental error, the curve fits the results except for one data point. This indicates that acetylacetone is ten times more reactive against positrons compared with benzene. The probability of *o*-Ps formation is however lower in the former case.

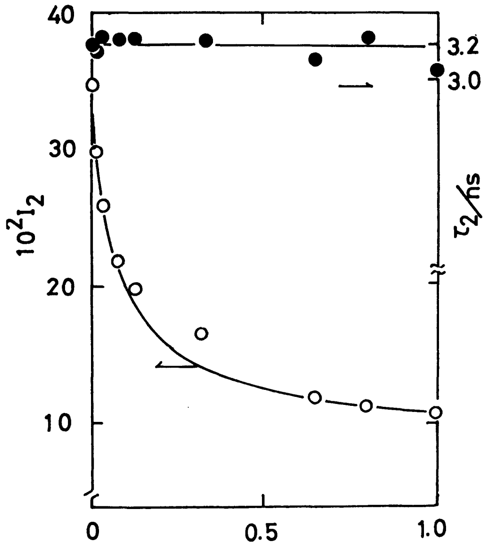


Fig. 1. Dependence of the lifetime(τ_2) and intensity(I_2) of *o*-Ps on the molar fraction of acetylacetone in acetylacetone–benzene mixture.

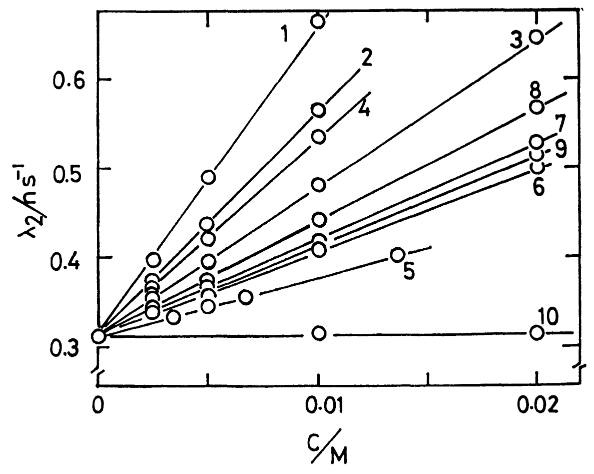


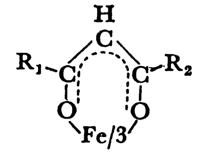
Fig. 2. Decay constant, $\lambda_2(\tau_2^{-1})$ of *o*-Ps in benzene solutions of β-diketonates of iron(III) as a function of the chelate concentration: (1) $Fe(hfa)_3$, (2) $Fe(tta)_3$, (3) $Fe(bta)_3$, (4) $Fe(tfa)_3$, (5) $Fe(dbm)_3$, (6) $Fe(bza)_3$, (7) $Fe(paa)_3$, (8) $Fe(acac)_3$, (9) $Fe(dpm)_3$, (10) $Al(bta)_3$ (as reference).

Effects of Ligating β-Diketonate Anion on the Lifetime of o-*Ps.* As reported in a previous paper,[12] $Al(dpm)_3$ and $Al(acac)_3$ do not affect the lifetime of *o*-Ps. Neither phenyl nor trifluoromethyl substituents changed the lifetime of *o*-Ps at 0.06 M, which was proved by the use of $Al(bza)_3$ and $Al(tfa)_3$. Therefore, the change in the lifetime of *o*-Ps in solutions of their complexes may be attributed to the effect of the central metal ions.

Lifetimes in Benzene Solutions of β-Diketonates of Iron(III) and Cobalt(III). The lifetime spectra of positrons and positronium were measured in benzene solutions of β-diketonato complexes at several concentrations. Figure 2 shows the plot of the observed decay constant, $\lambda_2(=\tau_2^{-1})$ against the solute concentration. For each compound, the following linear relationship was observed

$$\lambda_2 = 0.313 + k[\mathrm{C}],$$

where 0.313 is the pick-off rate constant of *o*-Ps in pure benzene, [C] the molar concentration of the complex, and k the rate constant for *o*-Ps decay induced by the solute. The observed rate constants are given in Table 1. Apparently, the acceleration of *o*-Ps decay is greatest for compounds which have the trifluoromethyl group in the ligands. The trend is clearly shown in Fig. 3, where the rate constants of β-diketonates with different substituents are compared. For a series of β-diketonates with one common substituent, the acceleration of *o*-Ps decay increased in the same sequence of the other substituents. The sequence is closely related to the electron attracting or releasing properties of the substituents. For a more quantitative estimation of the latter property, the cyclic voltammograms were measured in DMF. Typical voltammograms are shown in Fig. 4. The voltammogram of $Fe(dbm)_3$ showed an almost reversible wave, whereas those of the other iron(III) compounds were found to be irreversible; the



Common substituent	The sequence of the other substituent with regard to the acceleration of the *o*-Ps decay
CF_3	CF_3>thenoyl>CH_3>phenyl
phenyl	CF_3>CH_3>phenyl
CH_3	CF_3>CH_3>phenyl

Fig. 3. Schematic drawing of the molecular structure of tris(β-diketonato)M(III) (M=Co, Fe) and the sequence of the substituents with respect to the effects on the *o*-Ps decay.

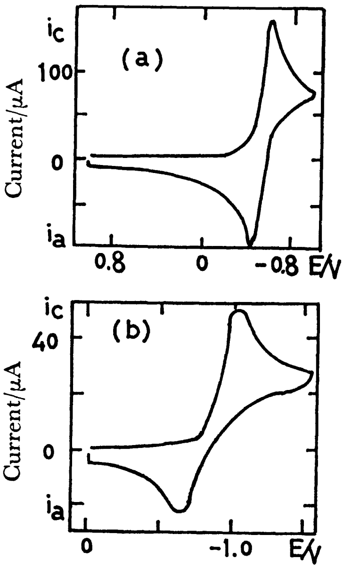


Fig. 4. Cyclic voltammograms for 5 mM β-diketonates of Fe(III) in *N*,*N*-dimethylformamide with 0.1 M tetrabutylammonium perchlorate: (a) $Fe(bza)_3$, (b) $Fe(dpm)_3$. Scan rate was 100 mV/s and the potential was measured against a saturated Ag/AgCl electrode.

Table 1. Rate constants of *o*-Ps reaction and the cathodic and anodic potentials of cyclic voltammograms for β-diketonates of iron(III) and cobalt(III)

	$10^{-9}\,k/M^{-1}\,s^{-1}$	$E_{pc}/V^{a)}$	$E_{pa}/V^{a)}$
$Fe(hfa)_3$	33.8 ± 0.8	0.50	0.72
$Fe(tta)_3$	24.6 ± 0.5	0.06	0.19
$Fe(bta)_3$	19.6 ± 0.5	0.07	0.21
$Fe(tfa)_3$	22.1 ± 0.7	0.00	0.19
$Fe(dbm)_3$	7.1 ± 0.4	−0.55*	−0.49*
$Fe(bza)_3$	9.6 ± 0.3	−0.61	−0.47
$Fe(paa)_3$	10.1 ± 0.4	−0.69	−0.55
$Fe(acac)_3$	15.6 ± 0.6	−0.68	−0.55
$Fe(dpm)_3$	10.5 ± 0.4	−1.16	−0.66
$Co(bta)_3$	16.6 ± 0.7	−0.07	1.12
$Co(tfa)_3$	17.0 ± 0.6	−0.05	1.10
$Co(bza)_3$	0.5 ± 0.1	−0.93	0.53
$Co(acac)_3$	1.1 ± 0.2	−1.04	0.47
$Co(dpm)_3$	0.0 ± 0.1	—b)	—b)

a) The scan rate was 100 mV/s except for the data with an asterisk for which the scan rate was 500 mV/s, and the reproducibility of the potential was within ±0.04 V on each sample. b) No reliable data were obtained because of the limited solubility of $Co(dpm)_3$.

irreversibility was highest for the wave of $Fe(dpm)_3$ among the iron(III) compounds studied, the results of which are summarized in Table 1. Figure 5 gives a plot of log *k* against *E*, the redox potential (the average of the peak potentials of the reduction and oxidation waves) of the complex. As expected, a greater acceleration of *o*-Ps decay was in general observed for a complex of less negative redox potential. The trifluoromethyl group tends to withdraw σ-electrons from the chelate ring, and therefore makes the reduction of the complex easier, both at the electrode and by *o*-Ps. Dipivaloylmethane has electron-releasing methyl substituents, and thus the increased electron density at the iron(III) atom of the dipivaloylmethanate makes the addition of an electron less easy. As seen in Fig. 5, exceptions were found for those compounds with phenyl substituents. In spite of the more positive or less negative redox potentials, the values of the rate constants were lower for $Fe(bta)_3$ and $Co(bta)_3$ than for $Fe(tfa)_3$ and $Co(tfa)_3$, respectively. The compounds, $Fe(dbm)_3$, $Fe(bza)_3$, $Fe(paa)_3$, and $Co(bza)_3$ also contain phenyl groups and showed lower *k* values than expected from the reduction potentials.

The *o*-Ps decay was also accelerated by most cobalt(III) complexes, but to a lesser extent than by the iron(III) analogues. This can primarily be attributed to the more negative reduction potentials of the cobalt(III) complexes. The reduction potential however cannot fully explain the very slow rate of reaction between *o*-Ps and the complex, and the electronic structure of the cobalt(III) complex may be partly responsible for the slow rates. Unlike the iron(III) β-diketonate of the high-spin type ($S=5/2$), all the cobalt(III) complexes investigated are of low-spin type ($S=0$). In the reduced state, however, the high-spin configuration should be preferred by the cobalt complexes ($S=3/2$) as well as the iron complexes ($S=2$). Thus, an extra activation energy will be required in the reduction of the cobalt complexes. Activation energy is essential in a kinetic process such as the reaction of *o*-Ps, but rarely important in the equilibrium. Voltammetry measures an equilibrium property rather than a kinetic one, although the latter is to some extent involved when irreversible waves occur. Thus the extra activation energy required in the reduction of cobalt(III) complexes will make the rate of the reaction with *o*-Ps considerably lower than expected from the redox potential.

An approximately linear relationship was observed between log *k* and *E* (Fig. 5); however, the slope or the value of $\Delta\log k/\Delta E$ was unusally small. A linear free energy relationship is often observed between logarithms of the rate and equilibrium constants of interrelated reactions, with a coefficient of $\Delta\log k_A/\Delta\log K_{A'}$, usually ranging from 0.3 to 0.9.[17] The $\Delta\log k/\Delta E$ value of 0.33

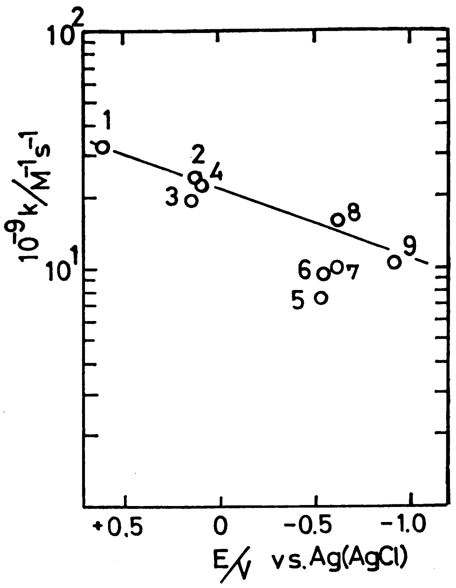


Fig. 5. Rate constants for the reactions of *o*-Ps with *β*-diketonates of iron(III) *vs.* the half-wave potentials measured with cyclic voltammetry in *N*,*N*-dimethylformamide with 0.1 M tetrabutylammonium perchlorate: (1) $Fe(hfa)_3$, (2) $Fe(tta)_3$, (3) $Fe(bta)_3$, (4) $Fe(tfa)_3$, (5) $Fe(dbm)_3$, (6) $Fe(bza)_3$, (7) $Fe(paa)_3$, (8) $Fe(acac)_3$, (9) $Fe(dpm)_3$.

observed here corresponds to a $\Delta\log k/\Delta\log K$ value of approx. 0.02.

No definite explanation can be made at present for this unusually small value. A possible explanation is that the rate constants were observed in a region where the rate is close to diffusion controlled. Assuming this to be the case, the $\Delta\log k/\Delta E$ value can be unusually small, but cannot be constant over such a wide range as covered in Fig. 5. Another possibility is that the difference between activation energies for the reactions of *o*-Ps and the iron(III) complexes is much less than that between the free energy changes for the electrode reactions of the complexes. This may occur if the structure of the complex undergoes only slight changes during the process of the reaction with the *o*-Ps atom, a very soft atom, from the initial to the transition state. A third possibility cannot be excluded, *i.e.* that the observed linear relationship is incidental and results from a mixing of the various effects including the steric effect of the substituent groups.

The acceleration of *o*-Ps decay can also occur through the spin-conversion mechanism in the presence of unpaired electrons. In the present case, this mechanism may not be important, since it has been previously shown that *o*-Ps decay by way of spin-conversion process makes only a minor contribution when both spin-conversion and oxidation processes are possible.[18]

The authors wish to thank Prof. I. Motoyama for his valuable advice on cyclic voltammetry.

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