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Annihilation of Positron and Positronium in Benzene Solutions of Lanthanoid Dipivaloylmethanates

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The lifetime of *ortho*-positronium(*o*-Ps) was measured in benzene solutions of several lanthanoid dipivaloylmethanates. None of the paramagnetic lanthanoid dipivaloylmethanates, Ln(dpm)$_3$ (Ln=Eu, Gd, Tb, Dy, Ho, Er, and Yb), accelerated the *o*-Ps decay (τ_2=3.2 ns). On the other hand, diamagnetic tetrakis(dipivaloylmethanato)cerium(IV), Ce(dpm)$_4$, shortened the lifetime of *o*-Ps (τ_2=1.9 ns for a 0.02 mol dm^{-3} solution in benzene). These results clearly indicate that the acceleration of the *o*-Ps decay by lanthanoid complexes occurs through the oxidation mechanism, not through the spin-conversion mechanism. This confirms the previous conclusion from experiments with 3d transition-metal β-diketonates that the oxidation of *o*-Ps is mainly responsible for the rapid *o*-Ps decay caused by the Fe(III) and Mn(III) complexes. Factors which influence the intensity and decay rate of *o*-Ps are discussed in connection with the experimental results.

The reaction of *ortho*-positronium(*o*-Ps) with inorganic ions in aqueous solutions has been studied by many investigators. Jackson and McGervey[1)] measured the lifetime of *o*-Ps in solutions of KMnO$_4$, HgCl$_2$, *etc.* and attributed the observed acceleration of *o*-Ps decay to the oxidation of *o*-Ps by the oxidizing ions. Ache and his coworkers[2–4)] observed no significant changes in the lifetime of *o*-Ps in aqueous solutions containing Sn(II), Pb(II), Cd(II), *etc.* up to a concentration of about 2 M. On the other hand, the intensity (I_2) of *o*-Ps decreased with an increase in the solute concentration and approached a saturation value characteristic of each solute. The results were explained in terms of hot Ps reactions with solute species.

Previously,[5–6)] we measured the lifetime of *o*-Ps in benzene solutions of 3d transition-metal acetylacetonates and dipivaloylmethanates, and showed that the decay rate of *o*-Ps was accelerated to a great extent by the Fe(III) and Mn(III) complexes and to a lesser extent by the Cu(II), Co(II), Co(III), and Cr(III) complexes, but that no acceleration was observed with the Al(III), Ni(II), and Zn(II) complexes. The complexes of the first group are oxidizing, those of the second group (except for the Co(III) complexes) are paramagnetic and poorly oxidizing, and the third-group complexes are non-oxidizing and diamagnetic. The conclusion was that, while the oxidation of *o*-Ps by oxidizing complexes proceeds very rapidly to result in a great acceleration of the *o*-Ps decay, the spin conversion of *o*-Ps through interaction with paramagnetic complexes proceeds slowly to result in a slight acceleration of the *o*-Ps decay.

The present study has been made with the intention of substantiating the previous conclusion and of determining the factors governing the rate of spin conversion. Lanthanoid dipivaloylmethanates were chosen for this purpose, since they show a series of different spin and total angular momenta (different quantum numbers, S and J) and since they include cerium(IV) dipivaloylmethanate, a unique compound which is diamagnetic and highly oxidizing.

Experimental

Lanthanoid tris(dipivaloylmethanato) complexes, Ln(dpm)$_3$, were prepared according to the procedure reported by Eisentraut and Sievers.[7)] The compounds were purified by repeated sublimations and by recrystallization from mixed benzene–hexane. Tetrakis(dipivalolylmethanato)cerium(IV) was synthesized by a method analogous to that presented for tetrakis(acetylacetonato)cerium(IV), Ce(acac)$_4$.[8)] The preparation of the dipivaloylmethanates of aluminium and 3d transition metals were described in a previous paper.[6)] The compounds were identified by elemental analyses. A definite amount of each compound was dissolved in distilled benzene. The solution was then placed in a Pyrex tube and degassed repeatedly by a vacuum freeze-thaw technique. About 6 μCi of ^{22}Na(NaCl) of a high specific activity was used as the positron source. The lifetimes of the positron and positronium were measured with a fast-slow coincidence system, the details of which have been described elsewhere,[9)] while the lifetime sepctrum was accumulated by means of a Hitachi 512-channel pulse-height analyzer. The time calibration was made by using coaxial cables of various lengths. The system as a whole gave a resolution (FWHM) of 750 ps for ^{60}Co prompt gamma rays and a 25 ns range of linear conversion.

Cyclic-voltammetric measurements were made of Ce(dpm)$_4$, Eu(dpm)$_3$, Fe(dpm)$_3$, Co(dpm)$_3$, Co(acac)$_2$, and Cu(dpm)$_2$ in dichloromethane(CH$_2$Cl$_2$) and partly in *N*,*N*-dimethylformamide(DMF), using 0.1 M tetrabutylammonium perchlorate(TBAP) as the supporting electrolyte. The measurement was carried out 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 calomel electrode, used as a reference, was connected to the cell by two salt bridges: a saturated KCl solution in water and a 0.1 M TBAP solution in CH$_2$Cl$_2$ (or DMF). A Hokuto Denko Model HA-101 potentiostat and a Hokuto Denko Model HB-107 function generator were used. The scan rate was 0.50 and 1.00 V/s, and voltammograms were recorded by means of a Rikadenki X-Y recorder, Model BW 133.

Results and Discussion

The lifetimes of *o*-Ps, obtained from the measured lifetime spectra, are listed in Table 1, together with the I_2 values. The obtained decay constant, λ_2, of *o*-Ps is plotted against the solute concentration in Fig. 1. None of the Ln(dpm)$_3$-type complexes (Ln=La, Gd, Tb, Ho, Dy, Er, and Yb) changed the lifetime of *o*-Ps in benzene, while Ce(dpm)$_4$ greatly accelerated the *o*-Ps decay. Since cerium(IV) has no unpaired electrons, the acceleration of the *o*-Ps decay by Ce(dpm)$_4$ can undoubtedly be attributed to its highly oxidizing nature, which was confirmed by cyclic voltammetry. The voltammograms of Ce(dpm)$_4$ and Fe(dpm)$_3$ in dichloromethane are compared in Fig. 2, while the E_{pc} values are listed in Table 2. It can be inferred from these results that Ce(dpm)$_4$ would be more oxidizing than Fe(dpm)$_3$ in benzene, too. Therefore, one might expect that *o*-Ps decay would be accelerated to a greater extent by the more oxidizing Ce(dpm)$_4$ than by the less oxidizing Fe(dpm)$_3$. However, experiments showed that the two complexes differed only slightly from each other in the rate constants for their reactions with *o*-Ps. This can be taken as demonstrating that the reaction is almost encounter-controlled in both cases.

TABLE 1. THE LIFETIMES AND THE INTENSITIES OF *o*-Ps IN 0.02 M BENZENE SOLUTIONS OF DIPIVALOYLMETHANATES OF LANTHANOID AND OTHER METALS

	λ_2/ns	$10^2 I_2$	Number of unpaired electrons[c]
Benzene	3.20±0.02	34.3	
Al(dpm)$_3$	3.03±0.02	31.9	0
Cr(dpm)$_3$	2.46±0.03[a]	32.0	3
Fe(dpm)$_3$	1.91±0.03	27.4	5
La(dpm)$_3$	3.23±0.03	31.3	0
Ce(dpm)$_4$	1.92±0.09	32.5	0
Eu(dpm)$_3$	3.21±0.03	32.0	6
Gd(dpm)$_3$	3.23±0.07	31.8	7
Tb(dpm)$_3$	3.16±0.02	32.8	6
Dy(dpm)$_3$	3.15±0.03	32.2	5
Ho(dpm)$_3$	3.16±0.03	32.2	4
Er(dpm)$_3$	3.22±0.03	31.5	3
Yb(dpm)$_3$	3.19±0.03[b]	32.6	1

a) A value for the 0.1 M solution. b) A value for the 0.03 M solution. c) Estimates from literature data on similar [MO$_6$]-type complexes.[14]

TABLE 2. DATA OF CYCLIC VOLTAMMETRY AND THE RATE CONSTANT FOR THE REACTION WITH *o*-Ps

	E_{pc}[a]	E_{pc}	$10^{-9}k$[c]
	V in CH$_2$Cl$_2$	V in DMF	M^{-1} s^{-1}
Cr(dpm)$_3$	−1.70[b]		0.66
Fe(dpm)$_3$	−1.32	−1.12	10.55
Co(dpm)$_3$	−1.70[b]	−1.32	0
Co(acac)$_3$	−1.28	−0.86	1.13
Co(acac)$_2$	−1.70[b]		0.99
Cu(dpm)$_2$	−1.70[b]		2.00
Ce(dpm)$_4$	−1.08		11.10
Eu(dpm)$_3$	−1.70[b]		0
Gd(dpm)$_3$			0
Tb(dpm)$_3$			0
Dy(dpm)$_3$			0
Ho(dpm)$_3$			0
Er(dpm)$_3$			0
Yb(dpm)$_3$			0

a) E_{pc}=Potential corresponding to the cathodic peak current (scan rate 0.5 and 1.0 V/s). b) The potential where the reduction of CH$_2$Cl$_2$ took place. c) k=rate constant for the reaction with *o*-Ps.

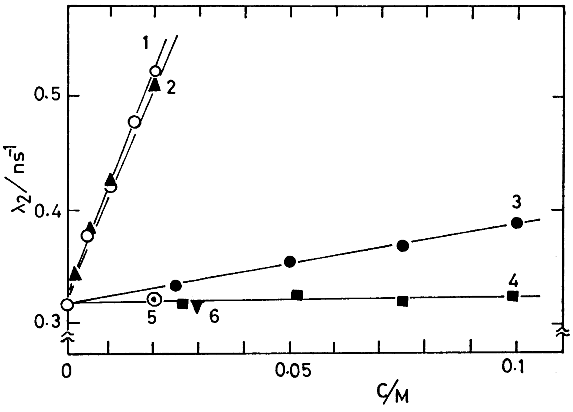

Fig. 1. Decay constant $\lambda_2(=\tau^{-1})$ *vs.* the solute concentration.
1: Ce(dpm)$_4$, 2: Fe(dpm)$_3$, 3: Cr(dpm)$_3$, 4: Al(dpm)$_3$, 5: Gd(dpm)$_3$, 6: Yb(dpm)$_3$.

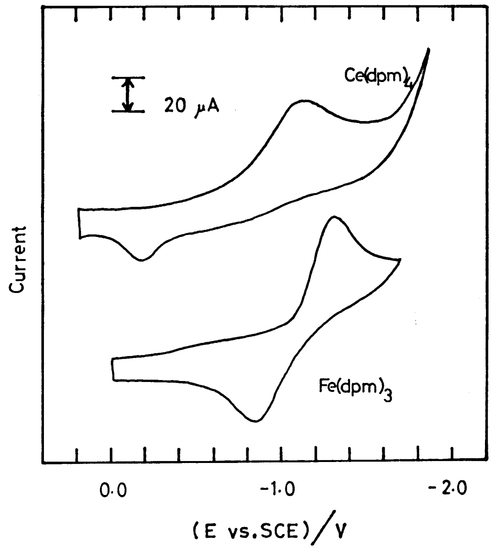

Fig. 2. Cyclic voltammograms for Ce(dpm)$_4$ and Fe(dpm)$_3$ in 0.1 M TEAP in CH$_2$Cl$_2$.

Tripositive europium ions are known to be easily reduced to a dipositive state. However, the normal λ_2 value observed for a Eu(dpm)$_3$ solution shows that the complex is not oxidizing enough. Consistently, the E_{pc} value for Eu(dpm)$_3$ was found to be more negative than the potential where the reduction of the CH$_2$Cl$_2$ solvent took place.

Unlike 3d-transition-metal complexes, the paramagnetic lanthanoid complexes did not accelerate the *o*-Ps decay. In order to find the reason for this dissimilarity, the spin-conversion mechanism of *o*-Ps decay will now be examined. Whenever spin exchange occurs between *o*-Ps and a metal complex with unpaired electrons, spin pairing will occur in the complex except when the partly filled shell has only one electron or hole. Thus, in order for spin exchange to occur, the kinetic energy of the *o*-Ps must at least counterbalance the spin-pairing energy. The latter is estimated to be about 2.5 eV for most lanthanoid complexes other than Gd(dpm)$_3$ ($\approx$3.9 eV), Ho(dpm)$_3$ ($\approx$3.5 eV), and Yb(dpm)$_3$ ($\approx$0).[10)]

The Oré theory[11)] shows that the most efficient formation of Ps occurs when the kinetic energy of a positron goes below the energy of the first excited level of the solvent (4.90 eV for benzene). Then, the kinetic energy of the positronium formed will be distributed mainly in the range below 2.46 eV; *i.e.*, (kinetic energy of positron) + (binding energy of positronium) − (ionization energy of benzene) = 4.90 + 6.80 − 9.24 = 2.46 (see Fig. 3).

	Oré diagram for positronium formation in benzene (eV)		Kinetic energy of positronium (eV)
Ionization energy (E_i)	9.24	———	6.80
Energies of the excited levels	6.99	Excitation collisions and Ps formation	4.55
	6.19		3.75
	4.90	——— Ps formation	2.46
$E_i - E_b$*	2.44	———	0

*) E_b: Binding energy of positronium

Fig. 3. Oré diagram of positronium formation in benzene and the kinetic energy of positronium.

The foregoing argument raises an expectation that the *o*-Ps decay would be accelerated by Yb(dpm)$_3$, which requires no spin-pairing energy. The experimental results, however, failed to show this. This leads to the conclusion that the lanthanoid complexes (at least Yb(dpm)$_3$, but not Ce(dpm)$_4$) fail to accelerate the *o*-Ps decay, not because of a matter of energy balance, but because of the inertness of the 4f unpaired electrons. Abundant evidence shows that the 4f orbitals of the lanthanoid ions are well shielded from the surrounding ions by the 5s—5p closed shell. Thus, the overlap of the 4f orbital with the *o*-Ps orbital can be expected to be negligibly small. The present experimental findings not only conform with the negligible overlap, but also indicate that there exist no appreciable long-range interactions that would result in spin exchange between the 4f and *o*-Ps orbitals.

The effect of Ce(dpm)$_4$ on the I_2 value was not so great as that of Fe(dpm)$_3$, and it was similar to that of other lanthanoid complexes. With the Oré model of Ps formation, this can be attributed to the fact that, because of its closed-shell electron configuration, Ce(dpm)$_4$ has a relatively small number of excited states compared with the number for Fe(dpm)$_3$. When a molecule has thinly distributed excited states, it will have small chance of being excited on collision with a positron. Therefore, in a Ce(dpm)$_4$ solution, the *o*-Ps formation can be expected to compete favorably with the excitation of the complex, thus resulting in an unaffected I_2 value.

According to the spur model,[12,13)] however, positrons combine with the electrons produced in the radiation spurs to form Ps. If an electron scavenger is present, the electron concentration in the spur will be reduced, and, therefore, a smaller amount of Ps will be formed. In the system investigated here, Ce(dpm)$_4$ is as strong an oxidizing agent or electron scavenger as Fe(dpm)$_3$, and should result in a reduced I_2. This is not consistent with the experimental results. If, however, the spur model is applicable to the present system, the observed inertness of Ce(dpm)$_4$ can be considered to show its slow rate of electron scavenging as compared with the rate of Ps formation.

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10) The values are estimated to be 2.4 eV ($^5D_1 \leftarrow {}^7F_0$) for Eu^{3+}, 3.9 eV ($^6P_{7/2} \leftarrow {}^8S_{7/2}$) for Gd^{3+}, 2.6 eV ($^5D_4 \leftarrow {}^7F_6$) for Tb^{3+}, 2.6 eV ($^4F_{9/2} \leftarrow {}^6H_{15/2}$) for Dy^{3+}, 3.3 eV ($^3F_2 \leftarrow {}^5I_8$) for Ho^{3+}, and 2.4 eV ($^2H_{11/2} \leftarrow {}^4I_{15/2}$) for Er^{3+} (*cf.* W. T. Carnall, P. R. Fields, and K. Rajnak, *J. Chem. Phys.*, **49**, 4412 (1968)).

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