Positronium formation and inhibition in binary solid solutions on Al(III) and Co(III) tris(acetylacetonates)

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Positron annihilation lifetime spectroscopy has been applied in mixtures and in solutions of solid Al(III), Al(acac)$_3$, and Co(III), Co(acac)$_3$, tris(acetylacetonates). For the solid solutions of Co(acac)$_3$ in Al(acac)$_3$, a strong inhibition of positronium formation is observed with increasing cobalt complex concentration, while there is no quenching of the positronium lifetime. In the solid mixtures the positronium formation probability decreases linearly with Co(acac)$_3$ concentration, while the positronium lifetime remains constant. The free volume model appears inadequate to explain the experimental results which are satisfactorily understood on the basis of the spur model.

1. Introduction

From the results on positronium (Ps) formation in various organic crystals either pure or with added impurities, general correlations have been established between the Ps yields and lifetimes and the free volumes present in the solids. Such kind of results were at the origin of the so-called free volume model, which proposes that Ps is formed and can be trapped in preexisting defects of the solid [1,2]. However, recent publications involving solid metal complexes and organic compounds have stressed the importance of the chemical properties of the compounds in relation to Ps formation [3–5].

Thus, preliminary studies on solid pyridines [3] and on a series of lanthanide acetylacetonates [4] and dipivaloylmethanates [5], performed using both positron lifetime spectroscopy (LS) and the Doppler broadening of annihilation radiation lineshape technique (DBARL), have shown that Ps was preferentially formed in compounds exhibiting a negative

charge stabilization at specific sites. These results also indicated that the positron annihilation parameters are sensitive to the liability of the solids to charge transfer processes. Furthermore, recent measurements on coordination and organometallic transition metal complexes of the nickel triad led to the conclusion that the conformation of the complex plays an important role in the interpretation of the experimental data [6]: the nature of both the central metal ion and the ligand must be taken into account. Regarding the ligand, the interpretation is complicated, due to the variety of the influencing parameters: chemical structure and composition, presence of charge transfer processes, electron distribution.

In liquid solutions, it is well known that such ions as Fe^{3+}, Co^{3+}, and Cr^{3+} or their complexes can inhibit Ps formation and/or quench the Ps lifetime in polar [7–9] and in nonpolar solvents [9–11], while others, like Al^{3+}, are rather inert [11]. More generally, it appears that in nonpolar solvents, both Ps formation and inhibition are more efficient than in the polar solvents. These findings have been well explained in terms of the spur model of Ps formation [12,13], which essentially suggests that Ps is formed in the terminal part of the positron track, by the re-

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action of this particle with electrons released by ionization of the medium. It is important to note that the validity of the spur model has also been advocated in various instances as regards the solid state (e.g., ref. [14]).

Although there is an abundant literature on these subjects on liquids [13], the first preliminary results on solid solutions were recently published by our group [15]. Our purpose in the present work was therefore to study binary solid solutions of $Co(acac)_3$ in $Al(acac)_3$, where acac stands for the acetylacetonates ligand, over a broad range of concentrations. The host aluminium complex in which Ps formation is very efficient can, to some extent, be assimilated to a "nonpolar solvent", while the guest cobalt complex, in which hardly any Ps is formed, can be considered as solute.

2. Experimental

The aluminium complex was prepared as reported by Young [16]. The characterization of the compound was made by using melting point measurements (567–568 K), infrared spectroscopy and X-ray diffraction. The cobalt complex, from Alfa Inorganics, was dissolved in benzene for purification by column chromatographic method, using cellulose as stationary phase.

The solid solutions, $Al_{1-x}Co_x(acac)_3$, were prepared by dissolving appropriate amounts of the Co and Al complexes in benzene, then evaporating slowly the solutions in the air at room temperature. Due to the isomorphism between the two compounds [17], the formation of true solutions of substitutional class was expected.

The solid mixtures were obtained by finely grinding selected amounts of the pure complexes. These mixtures were used as blanks to be compared with the solid solutions. The granulometry of the samples for both systems was systematically controlled between 0.044 and 0.062 mm by sieving the samples.

Owing to the very close similarity of the crystallographic parameters [17] and to the resolution of apparatus, the X-ray diffraction (Rigaku model 3134) spectra for pure aluminium and cobalt compounds were virtually identical; therefore, no difference could be found as well as in the various spectra concerning

to either the mixtures or the solid solutions.

The lifetime spectra were obtained using an ORTEC fast–fast coincidence circuit, with time resolution, from the ^{60}Co prompt curve, of 280 ps. Carrier-free $^{22}NaCl$, of approximately 4×10^5 Bq activity, sandwiched between two 3.5 μm thick foils of Mylar, was used as the position source. The measurements were carried out at 294 ± 1 K. Three spectra, at least, were counted for each sample.

The lifetime spectra were satisfactorily analysed in three components using the POSITRONFIT-EXTENDED program [18], leading to the intensities (I_i) and lifetimes (τ_i) of the various positron states: subscripts 1, 2, and 3 will refer to para-positronium (p-Ps), free positron and ortho-positronium (o-Ps), respectively. Parameters measured in the pure solid phases will be denoted by superscript "0". The source correction amounted to 10%. In all cases, τ_1 was fixed to 120 ps, the value for p-Ps self-annihilation. The ascription of the longest-lived component to o-Ps is based on previous results in solid metal β-diketonates: the experiments showed that when a long-lived component is present, with a lifetime in the range from 900 to 1600 ps, the corresponding width of the DBARL line was much narrower than in europium β-diketonates in which no long-lived component was observed [4,5].

3. Results and data analysis

3.1. Pure solid acetylacetonates

Crystallographic molecular volumes (V_m) [17] and LS parameters for pure $Al(acac)_3$ and $Co(acac)_3$ are collected in table 1. The long-lived component intensity in pure $Co(acac)_3$ is very low. Our experience with many other solid compounds has revealed that when the relative intensity falls below 5%, approximately, the associated lifetime shows a tendency to increase and it is less reproducible (note, for instance, the last point in fig. 2); therefore, little significance is ascribed to these parameters.

3.2. Mixtures of Co(III) and Al(III) acetylacetonates

In the case of binary mixtures, the three-component analysis of the LS spectra yields, merely, the o-

Table 1
Densities (ρ), crystallographic molecule volumes (V_m) and LS parameters for pure Al and Co tris(acetylacetonates)

Compound	ρ (g cm^{-3})	V_m (nm^3)	τ_2^0 (ps)	τ_3^0 (ps)	I_3^0 (%)
Al(acac)$_3$	1.22	0.431	433±25	1232±40	43.1±2
Co(acac)$_3$	1.43	0.418	328±13	1785±566	1.5±0.5

Ps lifetimes as measured in the pure Al compound (see fig. 1a) and the intensities are directly proportional to the mole fraction of the Al(acac)$_3$ crystallites of the mixtures. In the present case, as the densities of both Al(acac)$_3$ and Co(acac)$_3$ are very similar (table 1), the relative volume, V_r, practically identifies with the mole fraction of the Co complex, X, whatever the value for X. Therefore, the intensity, I_3, should linearly vary with X in proportion to the probabilities of forming Ps in the pure Al(acac)$_3$ compound, I_3^0(Al) from table 1, as:

$$I_3 = (1-X)I_3^0(\text{Al}) . \tag{1}$$

As shown in fig. 1b, the experimental data are in perfect agreement with this expectation, indicating that even though they are finely divided, the crystallites of the two compounds form two independent
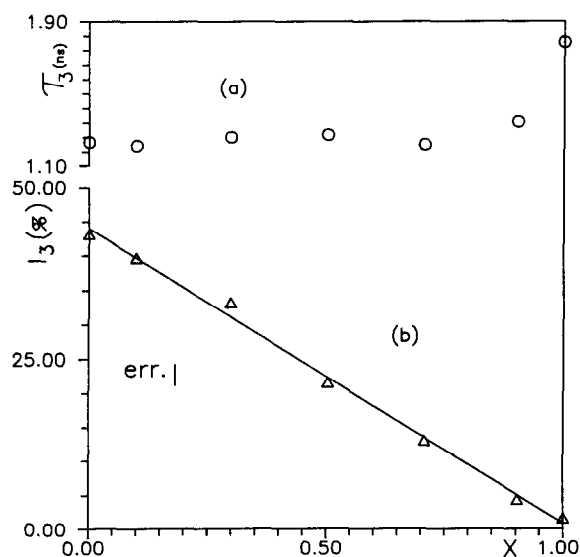
phases, with no interference on Ps formation from each other.

3.3. Solid solutions of Co(acac)$_3$ in Al(acac)$_3$

In contrast to what is found in the binary mixtures (fig. 1b), I_3 in the solid solutions decreases very rapidly with the increasing of the Co(acac)$_3$ mole fraction, becoming very small above $X=0.025$ (fig. 2b). Note that due to the low values of X at which I_3 can be determined, the molar concentration of Co(acac)$_3$ is very nearly a linear function of X.

Except for the value found at the highest mole fraction studied, which is poorly reliable due to the very small associated intensity, no important change appears to occur for τ_3 as a function of X (fig. 2a). The average value of τ_3 for $0 < X < 0.02$ is (1297 ± 88) ps,
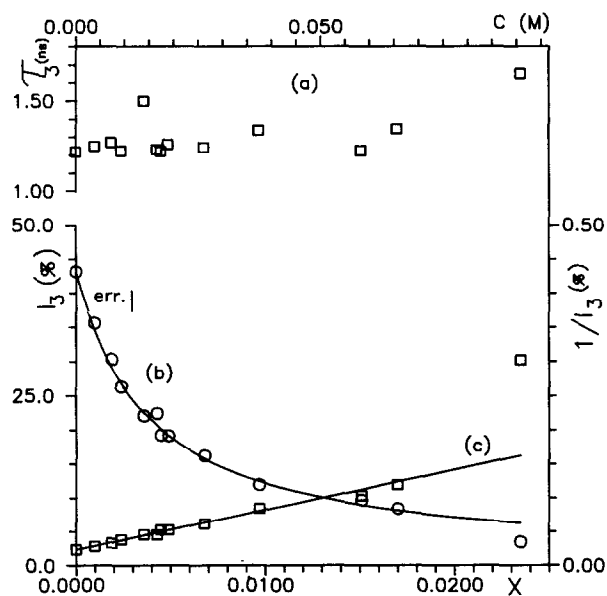

Fig. 1. Variation of τ_3 (a) and I_3 (b) with molar fraction (X) of cobalt in Co(acac)$_3$–Al(acac)$_3$ mixtures.

Fig. 2. Variation of τ_3 (a), I_3 (b) and $1/I_3$ (c) with molar fraction (X) and molar concentration of cobalt in solid solution Al$_{1-x}$Co$_x$(acac)$_3$.

which is somewhat higher, at the limit of experimental errors, than τ_3^0 (Al) as given in table 1. In any case, this shows that Co(acac)$_3$ does not promote any efficient Ps quenching reactions by oxidation mechanism nor by spin conversion once the Co(acac)$_3$ is a diamagnetic compound [10].

In the absence of any quenching reaction, I_3 directly represents the relative amount of o-Ps formed in the solid solutions [13]. The variation of $1/I_3$ with the molar concentration, C, of Co(acac)$_3$ is linear, in a similar way as found in many instances for liquid solutions [9,10,13]. In this case, the results can be fitted using the following equation:

$$I_3 = I_3^0 / (1 + kC) ,\qquad (2)$$

where k is the inhibition constant. A very good agreement is thus obtained with the experimental plot, for $k = 64 \pm 8$ M^{-1} (solid line in fig. 2b).

4. Discussion

4.1. Free volume model

According to the free volume model, the Ps intensity and lifetime should increase with increasing number and volume, respectively, of the voids present in the solid [1,2]. On this basis, it is important to examine some crystallographic data.

The X-ray diffraction data for Al(acac)$_3$ and Co(acac)$_3$ show that they are isomorphous, belonging to the monoclinic system, with four molecules per unit cell [16]. The volume of these cells are very close, at 1.722 and 1.672 nm^3, respectively, giving a total volume occupied by a single molecule (V_m), of 0.431 and 0.418 nm^3, respectively (table 1). The higher value of V_m for Al(acac)$_3$ while the radius of the central metal ion is smaller than in Co(acac)$_3$ arises primarily from the comparatively more ionic character of the aluminium–oxygen bonds [17]: this results in a stronger electrostatic repulsion between the oxygens, and, therefore, in a larger volume of the oxygen octahedron surrounding the Al ion. The corresponding measured and calculated densities (ρ) are very close in either case. This agreement indicates that the difference in ρ for the two compounds essentially stems from the masses of the central metal atoms, and therefore suggests that the two solids are structurally

very similar, with approximately the same free volume, V_f. Assuming that the annihilation rate of o-Ps inside the electron layer is 2 ns^{-1} [19], the size of V_f can be estimated by making use of the following equation, which has proven to be applicable to a large variety of molecular solids:

$$1/\tau_3 = 2[1 - r + (1/2\pi) \sin(2\pi r)] ,\qquad (3)$$

with $r = R/R_0$, where R is the radius of the voids in which the Ps survives and $R_0 - R = 0.166$ nm is the electron layer where it annihilates by pick-off. With $\tau_3^0 = 1.232$ ns for Al(acac)$_3$, a value of $R = 0.201$ nm and thus, $V_f = 0.0339$ nm^3 is derived. The latter is much smaller than $V_m = 0.431$ nm^3, showing that the voids in which Ps annihilates are not the intrinsic molecule vacancies. The intramolecular free spaces are also ruled out, because they are very small: thus, the crystallographic data [17] allow one to estimate at 0.023 nm only the radius of the free spaces available between the Al central ion and the oxygen planes in the octahedra constituted by the six oxygen ligands around this atom. Therefore, the voids in which Ps annihilates most probably correspond to the largest free spaces available in the lattice between adjacent Al(acac)$_3$ molecules.

From the preceding it appears that the free volume concepts alone are unable to explain most of our results on Ps formation and inhibition. Although they show that Co(acac)$_3$ occupies less space than Al(acac)$_3$, the crystallographic data indicate that the two compounds are structurally very similar. In particular, the free volumes available in either case are very probably too close to account for the drastic difference in the Ps formation probabilities (table 1). More strikingly, the model predicts an increase in I_3 when the Al(acac)$_3$ molecules are replaced by the somewhat smaller Co(acac)$_3$ molecules in the solid solutions, in contradiction to the experimental evidence.

4.2. Spur model of Ps formation

For instance, although it has proven to be very useful in some cases, the free volume model may be insufficient to describe Ps formation and in various solids the chemical properties of the lattice constituents should be closely considered [3,6]. In the present case, the validity of eq. (2) to describe the varia-

tion of I_3 with Co(acac)$_3$ concentration (fig. 2b), as observed in numerous cases in liquids [13], together with the well-known ability of the Co(III) compounds to scavenge electrons [20] strongly suggest an explanation of the results in terms of the spur model of Ps formation [12,13]. To sum up, the model proposes that Ps is formed by the reaction of the positron with one of the electrons produced by ionization of the medium at the end of the positron track. This reaction is in competition with other reactions between the radiolytic spur species, in particular, with the hole–electron recombination. Scavenging of the electrons by a solute leads therefore to the inhibition of Ps formation.

In liquids, where the model has been repeatedly shown to be valid, it is found that most of Ps formation arises from the reaction of the quasi-free electrons and positrons [13]; usually, inhibition in the presence of a solute is due to the scavenging of the former, and the variations of I_3 obey eq. (2) [13,21]. The efficiency of Co(acac)$_3$ as an inhibitor, measured through its inhibition constant (k), markedly increases when passing from polar to nonpolar solvents [8–10]: N-methylformamide ($k = 5.0$ M^{-1}) < methanol (10.4) < meta-cresol (14.5) < benzene (23.4). On this basis, it is quite feasible that k would be high in a solid molecular compound, resulting in a roughly threefold increase ($k = 64$ M^{-1}) as compared to benzene.

Very little information is available on Ps inhibition in solids. The inhibition constant of NO$_3^-$ is found to increase by a factor of only two in a glycerol–water mixture, when passing from the liquid to the glassy state [22], but this occurs at low temperature, below 200 K, where the mobility of the electrons might be importantly lowered. On the other hand, the reaction rate constants (k') of Ps with some selected solutes were found to increase by a factor of 2 to 4 in benzene and by a factor up to 30 in octanol when passing from the liquid to the solid (molecular) phases [23], close to the melting points. The inhibition constants are not reported by the authors but, as a general rule, high values of k' are always associated to high k values in polar solvents [13] (note that the reverse is not true), so that these ones are almost certainly very high too in the quoted frozen octanol solutions.

To a large extent, the higher probability of Ps formation and the correlated higher efficiency of non-ionic electron scavengers to inhibit this formation in non-polar comparatively to polar solvents that arise from two factors: (i) the much lower values of the dielectric constant in the former solvents, allowing longer range interactions between charged species; (ii) the presence of solvation processes in the polar solvents, which sets a temporal limit to the Ps formation reaction [13], as the solvated positron and electron have been repeatedly shown not to participate efficiently to this formation.

For the solid solution systems, however, although the absence of solvation processes is an important factor on Ps formation, it is certainly not the only one. Other factors, like created defects, anisotropy, chemical characteristics of the systems, may play a relative role in the mechanism of Ps formation as well. In comparison, the high value for $I_3^0 = 43.1\%$ in Al(acac)$_3$ related to $I_3^0 = 44.1\%$ [9,10] in liquid benzene stresses the importance of the absence of solvation processes in molecular solids concerning Ps formation.

In the solid solution, at mole fraction $X = 0.0043$ of Co(acac)$_3$, I_3 amounts to 22.4%, indicating that only about half of the Ps atoms initially formed in the matrix are left. At this mole fraction, the average distance between two Co(acac)$_3$ molecules can be estimated to be $d = 2[X^{-1} V_m(Al) \times 3/4\pi]^{1/3} = 5.76$ nm, which is almost 1.5 times higher than this value for a liquid solution of Co(acac)$_3$ in benzene of the same mole fraction. Therefore, it is quite surprising to find a so high efficiency of the Co(acac)$_3$ as a solute to scavenging the electrons on their way to form Ps, especially due to the solid state of our system.

Considering the high inhibition constant of Co(acac)$_3$ when diluted in Al(acac)$_3$, it is of course expected that I_3 would be close to zero in pure Co(acac)$_3$, as is experimentally observed, due to self-inhibition.

It thus appears that, as far as Ps inhibition but also Ps formation is concerned, the present results are quite compatible with an explanation in terms of the spur model. However, the precise reasons for the marked increase in the inhibition constants when passing from the liquid to the solid phases remain to be elucidated. The change in the electron mobility and the implication of solvation regarding both the electrons and the solute certainly play a role, but the pos-

4.3. Ps lifetime

The absence of any quenching effect of Co(acac)$_3$ on the Ps lifetime in the solid solutions appears somewhat surprising. In liquids, although the reaction of Co(acac)$_3$ with Ps has been repeatedly shown to be of a redox nature [8–10], the sequence of the absolute values of the reaction rate constant appears difficult to rationalize. Thus, the order at 294 K is different from that found for the inhibition constants: methanol ($k' = 0.35$ M^{-1} ns^{-1}) < benzene (1.4) < meta-cresol (2.3) < N-methylformamide (3.6). Even though the effects of the solvents on the solute are obviously involved, the importance of kinetic factors and the implication of reversible Ps–solute complex formation have been evidenced through the anomalous decrease of k' with increased temperature [9,10].

In solid Al(acac)$_3$ the thermodynamics of the problem is completely different, in particular because of the lattice energy, and it is possible that reduction of Co(III) by Ps would not be allowed. In fact, the o-Ps lifetime in the solid solutions appears to be slightly higher than in pure Al(acac)$_3$; this can be explained by considering that the free volume in the vicinity of the guest Co(acac)$_3$ molecules is somewhat larger than in the other lattice positions in the solid solutions, resulting in an increased o-Ps lifetime.

5. Conclusion

From the present study, it is confirmed that the free volume concepts may be quite insufficient to understand Ps behaviour in solids whenever some constituents of the lattice present marked chemical properties. Thus, the Ps formation probability and lifetime in Al(acac)$_3$, which is well known to be rather inert towards Ps in liquids [11], appear to be compatible with these concepts. But the very strong ability of Co(acac)$_3$ to inhibit Ps formation and the Ps formation probability in this compound when pure are in deep contradiction with the model.

The inhibition by Co(acac)$_3$ in the solid solutions fits very well in the general framework of the spur model, by considering the electron scavenging properties of this compound. Still, the causes of the important increase in the inhibition constant from liquid to solid solutions largely remain to be elucidated.

An important and practical result of this work is the demonstration, for the first time, of the possibility of using the positron annihilation techniques to characterize true solid solutions, by examining the positron behaviour in the solutions and comparing with the corresponding solid mixtures.

Further experiments are in progress at the laboratory to describe the limits of validity of the present conclusions in a variety of solid solutions and gain more information on the processes of electron scavenging in solids.

References

[1] Y.C. Jean, Microchem. J. 42 (1990) 72.
[2] T. Goworek, Phys. Stat. Sol. (a) 102 (1987) 511.
[3] A. Marques Netto, S.M.C.M. Bicalho, C.A.L. Filgueiras and J.C. Machado, Chem. Phys. Letters 119 (1985) 507.
[4] A. Marques Netto, S.M.C.M. Bicalho, J.C. Machado, E.O. Fantine, J.Ch. Abbé and G. Duplâtre, Chem. Phys. Letters 141 (1987) 198.
[5] A. Marques Netto, S.M.C.M. Bicalho, J.C. Machado, E.O. Fantine, J.Ch. Abbé and G. Duplâtre, in: Positron annihilation, 8th ICPA, eds. L. Dorikens-Vanpraet, M. Dorikens and D. Segers (World Scientific, Singapore, 1989) p. 815.
[6] S.I. Klein, R.S. Barbiere, A. Marques Netto, M.E.S.R. Silva and J.C. Machado, J. Braz. Chem. Soc. 1 (1990) 80.
[7] V.I. Goldanski, At. Energy Rev. 6 (1968) 3.
[8] G. Duplâtre, D. Kauffman and J.Ch. Abbé, in: Positron annihilation, 7th ICPA, eds. P.C. Jain, R.M. Singru and K.P. Gopinathan (World Scientific, Singapore, 1985) p. 190.
[9] W.F. Magalhães, Thesis, Université Louis Pasteur, Strasbourg, France (1987).
[10] W.F. Magalhães, J.Ch. Abbé and G. Duplâtre, Chem. Phys. 136 (1989) 141.
[11] K. Endo, M. Furukawa, H. Yamatera and H. Sano, Bull. Chem. Soc. Japan 53 (1980) 407.
[12] O.E. Mogensen, J. Chem. Phys. 60 (1974) 998.
[13] J.Ch. Abbé, G. Duplâtre, A.G. Maddock, A. Haessler and J. Talamoni, J. Inorg. Nucl. Chem. 43 (1981) 2603.
[14] O. Mogensen, Phys. Letters A 118 (1986) 357.
[15] J.C. Machado, C.F. Carvalho, W.F. Magalhães, A. Marques Netto, J.Ch. Abbé and G. Duplâtre, Mater. Sci. Forum 105–110 (1992) 1645.
[16] R.C. Young, in: Inorganic synthesis, Vol. 2, ed. W.C. Fernelius (McGraw-Hill, New York, 1946) p. 25.

[17] P.K. Hon and G.E. Pfluger, J. Coord. Chem. 3 (1973) 67.

[18] P. Kirkegaard and M. Eldrup, Computer Phys. Commun. 7 (1974) 401.

[19] H. Nakanishi and Y.C. Jean, in: Positron and positronium chemistry, eds. D.M. Schrader and Y.C. Jean (Elsevier, Amsterdam, 1988) p. 159.

[20] M. Anbar, M. Bambenek and A.B. Ross, Selected specific rates of reactions of transients from water in aqueous solution, 1. Hydrated electron, NSRDS-NBS-43 (US GPO, Washington, 1973).

[21] G. Duplâtre and C.D. Jonah, Radiat. Phys. Chem. 24 (1985) 557.

[22] G. Duplâtre, J.Ch. Abbé and J. Talamoni, in: Positron annihilation, 7th ICPA, eds. P.C. Jain, R.M. Singru and K.P. Gopinathan (World Scientific, Singapore, 1985) p. 233.

[23] V.P. Shantarovich, O.E. Mogensen and V.I. Goldanskii, Phys. Letters A 31 (1970) 485.