

The chemistry of positronium - Part VI : Inhibition and enhancement of positronium formation in aqueous solutions of halides, sulfide and thiocyanate.

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ABSTRACT

The formation of positronium in aqueous solutions of halides, sulfide and thiocyanate has been investigated. Inhibiting and enhancing reactions of positronium formation are found. The results are discussed in terms of the spur model.

INTRODUCTION

In previous papers of this series [1-5], we suggested that the positronium could be formed through two pathways, namely via (partially) solvated electrons and positrons or via the dry particles. About 30 % of the positronium would be formed according to the former process.

In the framework of the spur model [6] it might be expected that the scavenging of electron capturing entities such as OH[·] would increase the positronium yield. Trial experiments with 1M KI and KSCN solutions failed to reveal such an enhancement ($I_3/I_3^0 = 0.94$) [1] nor was it observed by Bertolaccini et al [7]. In view of these somehow unexpected data, measurements on halides, sulfide and thiocyanate solutions were repeated over a larger concentration range using lifetime spectroscopy.

The experimental technique and the computation processes have been described [1].

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RESULTS

The variations of I_3 , the intensity of the long-lived component, ascribed to o-Ps, as a function of I^- , Br^- , Cl^- , F^- , S^- , and SCN^- concentration are shown in figures 1, 2A and 2B. The salts were respectively NaI, NaBr, NaCl, KF, Na_2S and KSCN. The absence of an effect from the cation [7] was verified in the case of the iodide, by using NaI, KI and LiI. Only a very small, if any, variation of the lifetime τ_3 of the long-lived component, was observed. (The measurements were made up to 5M in the case of I^-).

Cl^- and F^- lead to saturation curves, but while the plateau value for Cl^- is of the same order of magnitude as that observed for H_{aq}^+ , it is much higher for F^- .

The curves relevant to I^- , Br^- , S^- and SCN^- exhibit minima.

The present results are in very good agreement with preliminary data obtained by Mogensen [8].

FITTING THE DATA

In the preceding two papers [4, 5] of this series the following semi-empirical relationship was used successfully for fitting the data :

$$\tau_3 = I_3^0 \frac{1}{1+k_2C} \left(\frac{f}{1+k_1C} + 1 - f \right) \frac{1}{1 - \frac{k_q}{1.96} C} \quad (I)$$

The last factor refers to quenching reactions with rate constants k_q , which can be deduced from the variation of $1/\tau_3$ versus C. The first two other factors in expression (I) are relevant to inhibition processes where k_1 and k_2 were tentatively assigned to the inhibition rate constants for the fraction of Ps formed, respectively, through (partially) solvated particles (fraction f) and dry entities.

It is clear that the above expression is no longer valid for fitting $I_3 = f(C)$ curves that exhibit a minimum. Such a behaviour reveals combined inhibiting and enhancing processes. As

stated previously [4], these new curves can be explained by multiplying expression (I) by a factor $(1 + \alpha C)/(1 + \beta C)$. Figure 2C shows the kinds of I_3-C curves that can arise if one includes enhancement. In the absence of any definite information on the actual mechanisms involved and in order to restrict the number of adjustable parameters, the following relationship was used to fit all curves :

$$I_3 = I_3^0 \frac{1 + \alpha C}{1 + \beta C} \left(\frac{f}{1 + kC} + 1 - f \right) \frac{1}{1 - \frac{g}{1.96} C} \quad (II)$$

The values of the parameters obtained for the solutes investigated in this work, as well as for NO_3^- are gathered in table 1.

It should be noted that the value of f depends drastically on precise determination of the experimental data and of the plateau value, this latter quantity requires measurements at high concentrations. However such measurements would not be acceptable because of possible direct radiolytic effects of the positron on the solute and changes in the solution properties.

In the case where α is not nil, parameters α , β and α/β should characterize the enhancing properties towards Ps formation of the solutions, β being related to the rate constant for scavenging the OH^\cdot by the solute, and $(\frac{\alpha}{\beta} - 1)$ representing the fraction of electrons which were being scavenged in the pure solution and are gradually released when the solute concentration is increased and participate in the formation of positronium. Here again, it can be seen that reliable values of α/β would demand that measurements be made at very high concentration, particularly in the case of low β values (Cl^- and F^-). Whenever α should be nil, β would be related to the reaction rate constant with either of the dry particles. Although it was not found to be the case with the solutes studied, it is not excluded that some ions may react, for instance, with all three entities : the damp positron, the OH^\cdot and the dry positron. Relation (II) would then require a further $(1/(1 + k_2 C))$ multiplying term accounting for the last process, but the experiments would have to be rather detailed and cover a large range of concentrations to reveal such processes.

DISCUSSIONS

As stated before, all the values of k_q are nil or very small, within the experimental errors. Thus the quenching reactions are negligible and they cannot account for the enhancement observed.

The f values are within the limits 0.2 to 0.31. Probably the value obtained for Cl^- solutions where the saturation plateau is clearly defined is the most relevant. This is in very good agreement with the hypothesis made previously that two processes are responsible for Ps formation with respective relative efficiencies of 30 and 70 %. We suggested that the first process involves (partially) solvated particles and the second dry e^- and e^+ . Recent experiments by Jansen and Mogensen [9] and Byakov et al [10] seem practically to exclude fully aquated electrons. Calculations on a kinetic model for Ps formation performed in our laboratory also lead to the same conclusion and in future we shall refer to this mechanism as involving damp electrons (e_d^-) or positrons (e_d^+).

From the table it appears that all the solutes are very strong positronium inhibitors except F^- . As all these anions are very weak electron (dry or damp) scavengers, the inhibition is attributed to the formation of the bound compounds (e^+X^-), for which there is experimental evidence, except for F^- [11, 12]. Recent calculations by Cade and Farazdel [13] show that these compounds are thermodynamically stable and the order of stability is $\text{F}^- > \text{Cl}^- > \text{Br}^- > \text{I}^-$. The very small reactivity of F^- is thus quite surprising. This may be due to the ion being very small and highly hydrated, a fact which would prevent interaction with the positrons.

Turning to the enhancement processes it appears that their importance decreases in the order $I^- > Br^- \approx SCN^- > S^{2-} > Cl^- > F^-$. It may be noticed that the SCN^- and Br^- ions are very similar in all respects (a similarity well known to inorganic chemists). It must be acknowledged that the parameters for F^- are less reliable, due to the low rate constant for damp positrons which would require very high concentrations of solutes for precise determination. No enhancement is found for NO_3^- . One can hypothesize that these ions trap the OH^\bullet radicals which results in an increase of free electrons and consequently of the probability of Ps formation. That radical scavenging occurs at higher concentration than e^- (or e^+) trapping is in good agreement with radiation chemistry results. Unfortunately the values of $k_{(OH^\bullet+F)}$ and $k_{(OH^\bullet+S^{2-})}$ are not available, but in fact the sequence of reactivities for the other ions towards OH^\bullet is the same as that for Ps enhancement. Another possible explanation is that these ions react with the precursor of the OH^\bullet radical, namely H_2O^+ , or other hole species, so that the enhancement parameters might reflect the hole scavenging rate constants. This would account for the observed inability of the OH^\bullet scavengers to increase $G(e_{aq}^-)$ 30ps [14] and would also tally better with the relevant time-scale, if only such early precursors as the damp (localized) and dry (unlocalized) positrons and electrons were involved in positronium formation.

The discovery of such a positronium enhancement process seems important support for the spur model for positronium formation.

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	α (M^{-1})	β (M^{-1})	α/β	f	k (M^{-1})	$k_q \times 10^{-9}$ ($M^{-1}s^{-1}$)
SCN ⁻	3.26	2.75	1.18	0.20	53.22	0.02
S ⁼	1.89	1.75	1.08	0.25	55.04	0.03
F ⁻	0.82	0.73	1.12	0.27	0.6	0
Cl ⁻	1.01	0.92	1.09	0.28	31.97	0
Br ⁻	3.23	2.75	1.18	0.27	52.64	0.022
I ⁻	5.07	3.68	1.38	0.31	55.49	0.029
NO ₃ ⁻	0	3.64		0.24	0.56	0

Table 1 : Values of the parameters deduced by fitting trial function (II) to the experimental data :

$$I_3 = I_3^0 \frac{1+\alpha C}{1+\beta C} \left(\frac{f}{1+kC} + 1-f \right) \frac{1}{1 - \frac{k_q}{1.96} C} \quad (II)$$

$(\alpha/\beta - 1)$: fraction of dry electrons released through OH[•]/hole scavenging.

β : ($\alpha \neq 0$) : related to the rate constant for OH[•]/hole scavenging.

($\alpha = 0$) : related to the rate constant for dry e⁺/e⁻ scavenging.

f : fraction of Ps formed through the reaction of damp e⁺/e⁻.

k : related to the rate constant for damp e⁺/e⁻ scavenging.

k_q : rate constant for quenching.

Fig. 1

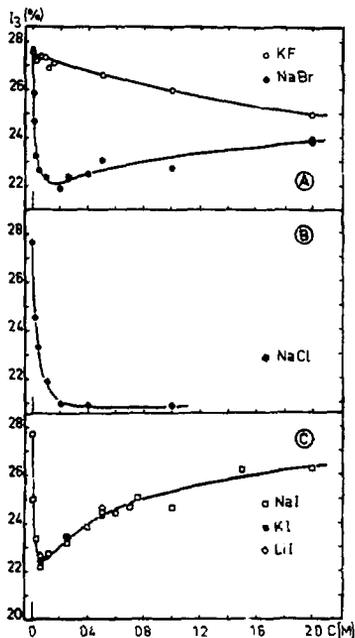


Fig. 2

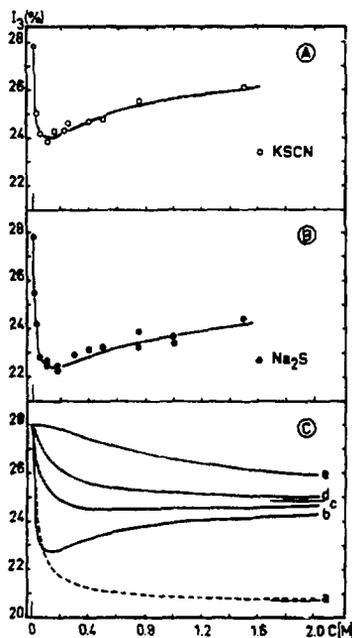


Figure 1 : Variations of I_3 , the o-Ps intensity, with concentration C of : (A), F^- and Br^- ; (B), Cl^- ; (C), I^- .

Figure 2 : Variations of I_3 , the o-Ps intensity, with concentration C of : (A), SCN^- ; (B), S^{2-} .

(C) : curves calculated from trial function (II), showing the effect of enhancement ($f = 0.26$ and $k_q = 0$ for all curves). No enhancement ($\alpha = \beta = 0$) and damp particle scavenging : (a) ($k = 30 \text{ M}^{-1}$) ; Constant enhancement ($\alpha/\beta = 1.2$; $\beta = 3 \text{ M}^{-1}$) and decreasing damp particle scavenging : (b) ($k = 55 \text{ M}^{-1}$) ; (c) ($k = 10 \text{ M}^{-1}$) ; (d) ($k = 4 \text{ M}^{-1}$) ; (e) ($k = 2 \text{ M}^{-1}$).