The chemistry of positronium - Part V : Inhibition of positronium formation by oxalic acid and oxalates in aqueous solutions

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Abstract

The inhibiting powers towards positronium formation of $H_2C_2O_4$, $HC_2O_4^-$, $C_2O_4^=$ and mixtures of these solutes in aqueous solutions have been measured. Whereas complete inhibition can be observed in solutions of the first two solutes, $C_2O_4^=$ yields only a limited decrease in the intensity of positronium. These results are discussed in terms of the spur model and of hot positron or positronium reactions.

1. Introduction

Radiolysis and pulse radiolysis experiments on oxalic acid and oxalates in aqueous solutions have been carried out by several authors and the rate constants for the reactions of hydrated electrons with the three forms of oxalic acid have been determined [1, 2].

In a previous paper we reported the rate constant for inhibition of positronium formation k by $C_2O_4^=$ anions [3]. We had found that the k values for some inhibitors were the same using aqueous solutions of either the acid or the neutral salt. On the basis of the "spur" model and taking into account the large differences between the $k_{e^-_{aq}}$ of the different species related to oxalic acid it seemed interesting to investigate the k values for each of these species individually, as well as for mixtures, by modifying the acidity of the solutions. These investigations were also instigated by the large difference in the positron affinities of $HC_2O_4^-$ and $C_2O_4^=$ calculated by SCHRADER and WANG [4].

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2. Experimental

The experimental device has been described previously [5]. Treatment of the data was performed as already stated by decomposing the curves into three exponentials. All values referring to water are characterized by the superscript 0.

Ph adjustments were made by additions of KOH to a 0,2 M $H_2C_2O_4$ solution.

3. Results

Due to the values of the dissociation constants of oxalic acid ($k_1 = 5.9 \times 10^{-2}$; $k_2 = 6.4 \times 10^{-5}$) [6] one cannot expect to study the effects of the pure oxalic acid molecule in water, at least at reasonable concentrations. It follows that figure 1a, which displays the variations of I_3 with oxalic acid concentration, corresponds to a composite curve wherein both the effects of the $H_2C_2O_4$ molecule and that of the $HC_2O_4^-$ ion are present.

On the other hand, the inhibiting effects on positronium formation of the $HC_2O_4^-$ and $C_2O_4^=$ ions, respectively, as shown in figure 1b, may be considered as directly representing the effects of these anions. The concentration range investigated for $HC_2O_4^-$ is unfortunately limited because of the low solubility of the salt. In no case was a significant variation of τ_3 observed.

The data indicate that whereas the $H_2C_2O_4$ molecule and the $HC_2O_4^-$ ion certainly belong to the group of inhibitors which follow the relationship (I) $I_3 = I_3^0 \frac{1}{1+kC}$, where C is the solute concentration, the $C_2O_4^=$ ion has to be included in the group of substances leading to partial inhibition. This last result is partly incompatible with the k value published in the second paper of this series which resulted from an incomplete investigation of the concentration range.

The variations of I_3 with pH in a 0.2 M $H_2C_2O_4$ solution are shown in figure 2.

4. Discussion

a) Fitting the data

The experimental data have been analyzed firstly in terms of an extension of equation (IV) from our previous paper [7] to a system containing two inhibitors of the nitrate type, $H_2C_2O_4$ and $HC_2O_4^-$, and one, $C_2O_4^=$, which apparently behaves like chloride :

$$(II) \quad I_3 = I_3^o \left(\frac{f}{1 + k'_1 C_1 + k'_2 C_2 + k_3 C_3} + \frac{1 - f}{1 + k_1 C_1 + k_2 C_2} \right)$$

Subscripts 1, 2 and 3 refer to $H_2C_2O_4$, $HC_2O_4^-$ and $C_2O_4^=$, respectively. It may be observed that k_1 and k'_1 on one hand and k_2 and k'_2 on the other part in the most general case could be different. However, as was found for the nitrate [7], it appears by fitting the data, that $k_1 = k'_1$ and $k_2 = k'_2$. The results were :

Species	$H_2C_2O_4$	$HC_2O_4^-$	$C_2O_4^=$
k for inhibition (M^{-1})	3.25	1.02	3.39
$k_{(e^-_{aq}+S)}$ ($M^{-1}s^{-1}$)	2.5×10^{10}	3.4×10^9	1.7×10^7 [*] 4.8×10^7

The proportion f of positronium liable to oxalate anion inhibition, expressed as a percentage of the total o.Ps production, is 22 %, a very similar value to that found for chloride [7], hydrogen ion [8] and silver and cadmium ions [9] as inhibitors.

It will be noted that the inhibiting powers of the oxalic acid and of the hydrogenoxalate anion parallel their reaction rate constants with aquated electrons and therefore, quite likely, their reaction rate constants with dry electrons [10]. The oxalate anion however does not readily capture electrons and

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[*]Two rather discordant values have been reported.

it would seem more reasonable to attribute its limited inhibition
to the reaction :

$$e^+_{aq} + C_2O_4^= \longrightarrow Ps\ C_2O_4^-$$
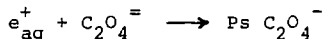
analogous to the chloride process [7, 11].

As was the case for NO_3^-/Cl^- mixtures [7], relation (II)
must be reconsidered if the hydrogenated forms and the $C_2O_4^=$ ion
do not react with the same species, as :

$$(III) \quad I_3 = I_3^O\ \frac{1}{1 + k_1C_1 + k_2C_2}\ (1 - f + \frac{f}{1 + k_3C_3})$$

The results were practically identical using either relation (II)
or (III) for fitting the data.

It should be mentioned that an attempt was made to
convert the inhibitors concentrations to activities by making use
of the sodium malonate mean activity coefficients [12]. Slight
improvements in the fitting curves were thus obtained, without
significant changes in the parameters values.

Summarizing our data on inhibition, it would seem that
those solutes leading to limited inhibition prevent the formation
of positronium from solvated (or partially solvated) positrons
either by reaction with the positrons, followed by annihilation
at much the same rate as the aquated positron. This class inclu-
des chloride and, perhaps, oxalate. Or the inhibitor scavenges
the aquated electrons, also necessary for positronium formation
in this way. The latter group probably includes hydrogen ion and,
for part of their action, silver and cadmium ions [9]. The normal
production of o.Ps in aqueous media through the solvated positron
would seem to amount to about 7 - 9 %.

The other mechanism of inhibition would appear to be
faster process, probably involving interference with positronium
formation of dry electrons and positrons in the terminal spur.

This category which includes nitrates, the haloacetates and apparently the oxalic acid molecule and the hydrogenoxalate anion shows some differences in the precise concentration dependence of the inhibition.

However, nothing that has been considered above excludes an explanation in terms of hot reactions of either positrons or positronium atoms. There must always be a hot reaction analogue of an electron or positron scavenging process. But a quantitative examination of this alternative may lead to improbable parameters.

b) Hot atom interpretation

It has been shown in a previous paper [7] that the classical Estrup-Wolfgang analysis cannot be applied to mixed solutions containing chloride and nitrate and the suitability of this treatment to hot positronium reactions has been questioned.

For the oxalate solutions it is in fact possible to fit the data to the expression derived previously [7]

$$- \frac{1}{\ln I_3^o/I_3} = \frac{1}{u} = \frac{\sum_i \frac{1}{1 - u_i A_i} + (1-n)}{\sum_i \frac{u_i}{1 - u_i A_i}}$$

with the parameters

$$A_1 = 4.11 \quad \text{and} \quad B_1 = 1.12 \quad \text{for} \quad C_2O_4^=$$
$$A_2 = 1.72 \quad \text{and} \quad B_2 = 0.67 \quad \text{for} \quad HC_2O_4^-$$
$$A_3 = 0.26 \quad \text{and} \quad B_3 = 0.30 \quad \text{for} \quad H_2C_2O_4$$

Since the moderating properties of the different oxalate species can hardly be very different, the A values would imply large differences in reactivity integrals. Such an analysis could be significant if hot positron reactions were concerned. But SCHRADER and WANG calculate [4] a substantial positron attachment energy for

$C_2O_4^=$ so that there seems no reason for a hot reaction.

Indeed the concept of a hot positronium reaction with a reducing entity like oxalate seems questionable. Further the inhibiting power of $H_2C_2O_4 > HC_2O_4^- > C_2O_4^=$, and it is hard to find reason for substantial changes in either hot positron or positronium reactivity with such a sequence.

5. Conclusions

Although these data still permit some unspecified hot positronium or positron reactions as an explanation of inhibition, an explanation in terms of dissociative electron scavenging by $H_2C_2O_4$ and $HC_2O_4^-$ together with solvated positron scavenging by $C_2O_4^=$ seems the more simple explanation of the data.

The substantial difference in the behaviour of $H_2C_2O_4$ and $HC_2O_4^-$ is noteworthy. It has been suggested that differences in the reactivities of the two species towards e_{aq}^- are due to the carbonylic groups rather than to the carboxylic hydrogen [13]. Further data on the inhibiting power of conjugated and non-conjugated double bonded molecules are being obtained.

It would appear important to explore whether addition of $C_2O_4^=$ to a nitrate inhibited solution has a similar effect to chloride [11] in giving rise to a narrow line component in angular correlation experiments.

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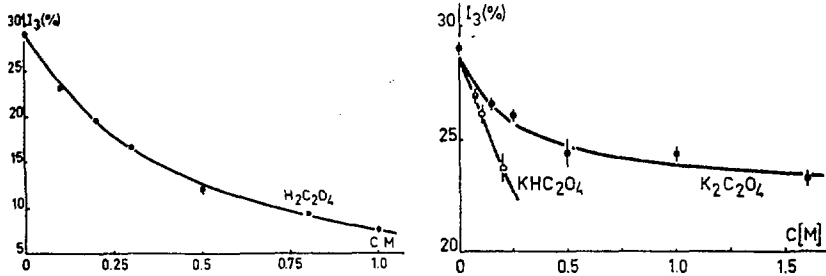   (1970)

Fig. 1 -   Variations of the intensity of o.Ps, I_3, with the
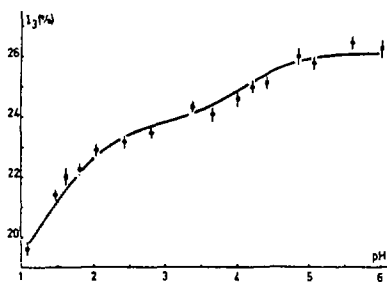concentration of $H_2C_2O_4$ (a), $HC_2O_4^-$ and $C_2O_4^=$ (b).

Fig. 2 -   Variations of the intensity of o.Ps, I_3, with the
pH in a 0.2 M $H_2C_2O_4$ solution.