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THE EFFECT OF PYRIDINIUM ION ON POSITRON ANNIHILATION IN AQUEOUS SOLUTIONS

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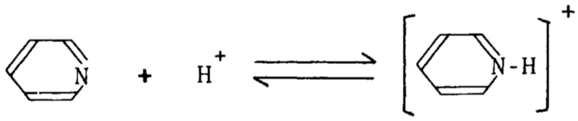
Positron lifetime measurements in aqueous solutions of pyridine-hydrochloric acid at various solute concentrations revealed that pyridinium ion, formed by Py + $H^+ \rightleftharpoons [PyH]^+$ reduced the relative intensity of ortho-positronium(I_2) without changing ortho-positronium lifetime(τ_2) significantly. Comparison of the result with that of anilinium ion suggested that the presence of pyridine ring, whose π electron density is lower than that of benzene, is an important point for the reduction of I_2.

The interaction of ortho-positronium(o-Ps) with many diamagnetic organic molecules in organic solvents was studied by Gol'danskii and Shantarovich,$^{1)}$ and Madia et al.$^{2)}$ Comparing the quenching rate constants of many molecules, they found that the quenching ability of organic molecules depends strongly on the existence of benzene ring whose π electron density is lower than that of benzene. Indeed a correlation was found between o-Ps quenching rate constants and Hammett's constants.

Pyridine is known not to be a quencher or an inhibitor of positronium in organic solvents,$^{3)}$ whereas positronium is rather difficult to form in pure pyridine(I_2= 9.3%).$^{4)}$ In aqueous acid solution, pyridine captures a proton to form a pyridinium ion,



(1)

and

$$K = \frac{[\text{Pyridinium ion}]}{[\text{Pyridine}][H^+]} = 1.58\times10^5. \qquad (2)$$

The presence of nitrogen in pyridine causes localization of electrons in heterogeneous ring. This tendency is expected to be strengthened by the protonation reaction (1) in aqueous solution of pyridine and mineral acid, therefore o-Ps quenching by pyridinium ion will be observed. The purpose of present study is to test this prediction experimentally by using positron lifetime technique. Lifetime spectra in aqueous solutions of pyridine, of pyridine-hydrochloric acid(ratio of molar concentrations—1:0.96), and of aniline-hydrochloric acid(1:0.93) were measured at various concentrations of the solutes.

The positron lifetime spectrometer employed is a usual fast-slow coincidence system which mainly consists of ORTEC units. Two detectors are NE111 plastic scintillators optically coupled to RCA8575 photomultiplier tubes. Time resolution of the system calibrated by a ^{60}Co source was 540 psec FWHM. After about 20ml of the sample solution was taken in a weighing bottle(ϕ38mm), about 7.5 μCi of carrier free ^{22}Na was added as a positron source. To remove oxygen, N_2-bubbling was carried out.

All of reagents used were of guaranteed grade and were used without further purification. All of the spectra were resolved into two lifetime components by using computer program 'POSITRON FIT EXTENDED' written by Kirkegaard and Eldrup.5) About 3.7% of positrons annihilating in the glass wall of the weighing bottle was corrected. Our results are shown in Figs.1 and 2.

Contrary to our expectation, pyridinium ion does not quench o-Ps strongly in aqueous solutions. Instead, remarkable reduction of I_2 is observed while anilinium ion causes only a little reduction. To represent quantitatively this inhibition effect, we fitted our results to the following formula used by Eldrup et al.6)

$$I_2 = I_0\left(0.85 + \frac{0.15}{1 + 60[\mathrm{Cl}^-]}\right)\left(\frac{1}{1 + \sigma[\mathrm{M}]}\right) \qquad (3)$$

where σ is a fitting parameter and is called as an inhibition coefficient, I_0 is an intensity of the long lifetime component in pure water, and [M] is a concentration of the solute. The term in the first parenthesis represents inhibition by Cl^-.

Several mechanisms for inhibition of positronium have been proposed. Tao and Green7) proposed a hot positronium reaction mechanism. They attributed the reduction of I_2 to a reaction of non-thermalized positronium with the solute. Mogensen8) proposed a spur model attributing the reduction of I_2 to the scavenging of dry or hydrated electrons by the solute in the positron spur. At present we cannot give a definite interpretation on the inhibition effect of positronium by pyridinium ion, since the reaction rate constants of pyridinium ion with dry or hydrated electrons are not available. However by comparing the result of pyridinium ion with that of anilinium ion, we may make a guess that the inhibition by pyridinium ion is correlated with the fact that the pyridinium ion has a ring whose π electron density is lower than that of benzene. Therefore pyridinium ion would react with hot positronium or, dry or hydrated electrons and cause a remarkable reduction of I_2. The agreement of inhibition coefficient of pyridinium ion($5.0M^{-1}$) with that of 1-pyridinium-propane-sulfonate-3'($5.85M^{-1}$) reported by Jansen et al.[9] also suggests an importance of such a pyridine ring, for both compounds have similar rings.

The reason why pyridinium ion does not quench o-Ps efficiently cannot be derived from the present experiment alone.

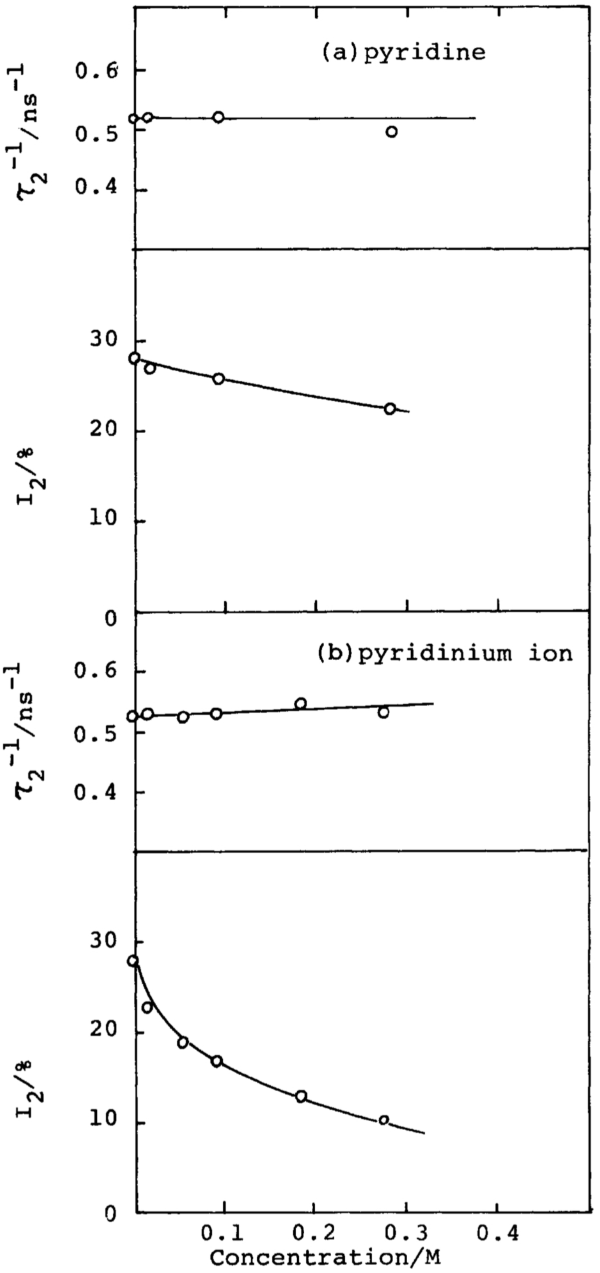


Fig.1 Dependence of I_2 and τ_2 on the concentration of pyridine and pyridinium ion. The standard deviation of each I_2 is less than 0.4%(absolute %). The solid line shows a fitted curve.

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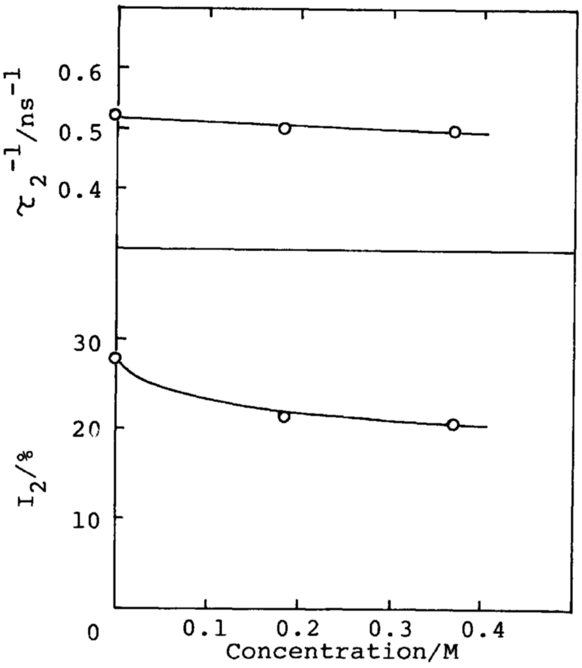

Fig.2 Dependence of I_2 and τ_2 on the concentration of anilinium ion. The standard deviation of each I_2 is less than 0.3%(absolute %). Solid line: fitted curve.

Table 1 Quenching rate constants and inhibition coefficients obtained from the lifetime spectra.

solutes	quenching* rate constants / $M^{-1}ns^{-1}$	σ / M^{-1}
Pyridine	——	0.85
Pyridinium ion	0.08	5.0
Anilinium ion	——	0.42

*Calculated from the equation that

$$k=\frac{\tau_2^{-1}-\tau_0^{-1}}{[M]}.$$

k :quenching rate constant,

τ_2 :measured lifetime of long-lived component,

τ_0 :o-Ps pick-off annihilation lifetime in water,

[M]:concentration of the solute.

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