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Effect of Protonation of Nitrogen-Containing Organic Molecules on the Reactivity toward Positronium

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Abstract: Positron lifetime parameters in aqueous or methanol solutions of pyrimidine, quinoline, and quinoxaline were determined with and without hydrochloric acid. By analyzing the data, the Ps reaction rate constant k and the Ps inhibition coefficient σ of free molecules and protonated cations were determined. The protonation of these molecules enhances k and σ considerably. The qualitative considerations suggest that the complex formation reaction between Ps and the protonated cations is responsible for the increase of k by protonation.

I. Introduction

The bound state between a positron and an electron, positronium (Ps), can exist in one of the two ground states, i.e., *o*-positronium (*o*-Ps) and *p*-positronium (*p*-Ps). The total angular momentum of *o*-Ps is $\hbar$ and that of *p*-Ps is 0. In free space, *o*-Ps annihilates into three γ quanta with a lifetime of 140 ns and *p*-Ps annihilates into two γ quanta with a lifetime of 0.125 ns. As Ps resembles the hydrogen atom, it can undergo chemical reactions by which its lifetime is shortened. It is well known that Ps is reactive toward inorganic oxidizing agents ($Cr_2O_7^{2-}$, MnO_4^-, IO_4^-, Tl^{3+}, Fe^{3+}, etc.)[1] and organic electron acceptors (nitrobenzene, quinone, tetracyanoquinodimethane, etc.).[2,3]

Up till now, several investigators have studied the effect of complex formation of these inorganic and organic species on their reactivities toward Ps. Lévay et al.[4] and Jansen et al.[5] studied the effect of the charge transfer complex formation of electron acceptors with electron donors. They found that electron acceptors taking part in the complex formation have smaller Ps quenching rate constants and larger Ps inhibition coefficients than those of the uncomplexed electron acceptors. Ache et al.[6,7] and Endo et al.[8] investigated the effect of complex formation of metal ions. They found that the effectiveness of the complexes to quench Ps varies depending on the chemical character of the complexes.

Recently the present authors[9] studied the effect of protonation of "chemically inert" pyridine and observed Ps inhibition by pyridinium ion. This Ps inhibition without Ps quenching was thought to be caused by the change in the local electron distribution in the pyridine ring.

The effect of protonation of nitrogen-containing organic molecules on the reactivity toward Ps was further studied through the positron lifetime measurements in aqueous solutions of pyrimidine and quinoxaline, in methanol solutions of quinoline, and in 1:1 aqueous solutions of pyrimidine, quinoxaline, and quinoline with hydrochloric acid.

II. Experimental Section

Apparatus. Positron lifetime spectra were measured in the usual way by determining the time interval between the detection of a

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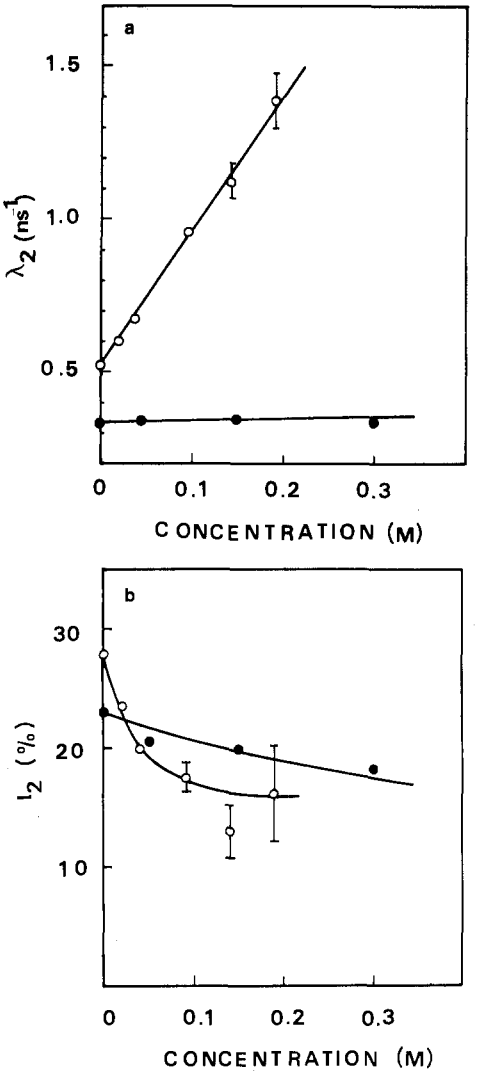


Figure 1. Concentration dependence of λ_2 (a) and I_2 (b) in the solution containing quinoline: ●, methanol solutions; ○, aqueous solution with HCl (1:1).

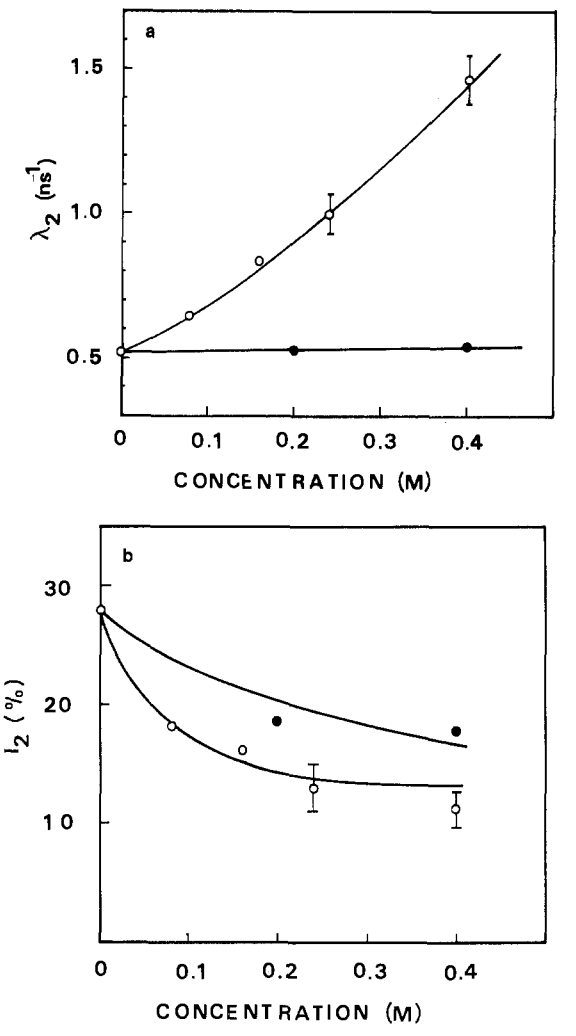


Figure 2. Concentration dependence of λ_2 (a) and I_2 (b) in the solution containing pyrimidine: ●, aqueous solution; ○, aqueous solution with HCl (1:1).

1.28-MeV photon of ^{22}Na emitted simultaneously with the birth of a positron and the detection of a 0.511-MeV annihilation photon. The apparatus used was a usual fast–slow coincidence system which mainly consists of ORTEC units. Two detectors were NE111 plastic scintillators optically coupled to RCA8575 photomultiplier tubes. The time resolution of the system was measured by using a ^{60}Co point γ source and proved to be 540 ps fwhm.

Positron Lifetime Measurements. Reagents were purchased from Tokyo Kasei Kogyo or Kanto Chemical Co., Inc., and were used without further purification. After about 20 mL of the sample solution was taken in a weighing bottle, about 7.5 μCi of ^{22}Na (as ^{22}NaCl) was added as the positron source. Dissolved oxygen was removed by bubbling the nitrogen gas through the solution.

Data Analysis. The lifetime spectra were resolved into two lifetime components by using the POSITRON FIT EXTENDED program written by Kirkegaard et al.[10] The time resolution function was determined by measuring a prompt curve of $^{60}CoCl_2$ in aqueous solution prepared and placed in the same conditions as the sample solutions without changing the energy window setting of the SCA. The curve was approximated as a sum of Gaussians.

The contribution of the positrons annihilating in the glass wall of the weighing bottle was estimated by measuring first the positron lifetime spectrum of the glass and secondly that of 0.2 M $KMnO_4$ aqueous solution. Determined "source component" was τ_1 (lifetime of the short-lifetime component) = 0.44 ns, τ_2 (lifetime of the long-lifetime component) = 1.29 ns, I_2 (intensity of the long-lifetime component) = 32.1%, total intensity = 3.7%. This component was corrected in the course of data analysis.

III. Results

The concentration dependences of the *o*-Ps annihilation rates (λ_2) and their relative intensities (I_2) are shown in Figures 1–3. Undoubtedly the addition of HCl changes the concentration dependences of the *o*-Ps annihilation rates. For all solutions investigated, in the absence of HCl, λ_2 changes only a little with increasing the solute concentration. In the presence of HCl, λ_2 increases remarkably with the solute concentration. Such a behavior suggests that the chemical reaction of *o*-Ps proceeds in the solutions with HCl, because no paramagnetic species are present in the solution and the contribution of ortho-para conversion of Ps is not expected.

IV. Analysis of the Data

When the chemical reaction of *o*-Ps is present, the theoretical positron lifetime spectrum, $N(t)$, is expressed as,

$$N(t) = \frac{1}{4}P\lambda_s e^{-\lambda_s t} + \lambda(1-P)e^{-\lambda t} - \frac{3}{4}P\frac{\lambda_q\lambda}{\lambda-(\lambda_p+\lambda_q)}e^{-\lambda t} + \frac{3}{4}P\frac{(\lambda-\lambda_p)(\lambda_p+\lambda_q)}{\lambda-(\lambda_p+\lambda_q)}e^{-(\lambda_p+\lambda_q)t} \quad (1)$$

where P is the Ps formation probability, λ_s is the self-annihilation rate constant of *p*-Ps, λ is the mean annihilation rate constant of the positron that does not form Ps ($\lambda = 2.5 \times 10^9$

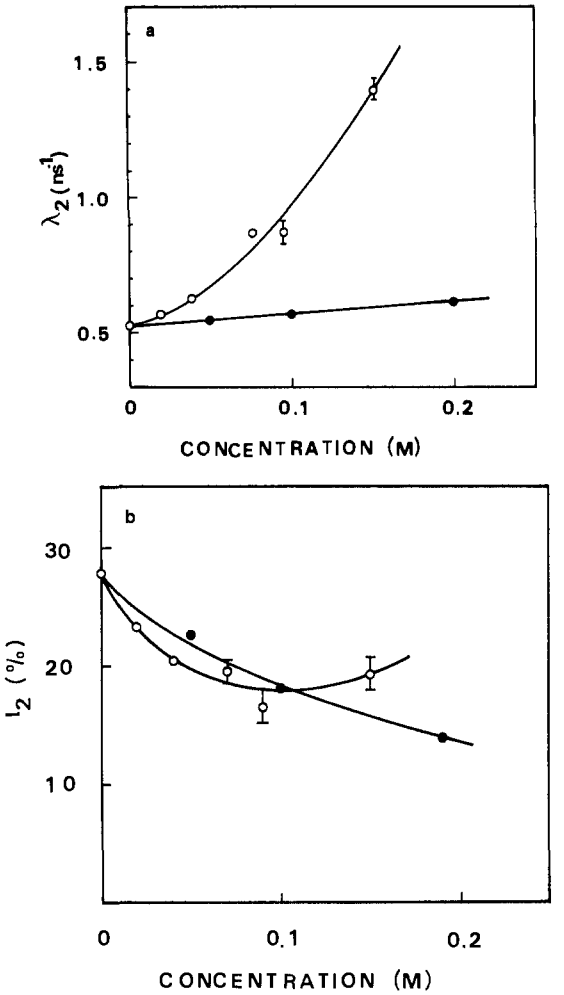


Figure 3. Concentration dependence of λ_2 (a) and I_2 (b) in the solution containing quinoxaline: ●, aqueous solution; ○, aqueous solution with HCl (1:1).

s^{-1}),[11] λ_p is the pick-off annihilation rate constant of *o*-Ps in the pure solvent, and λ_q is the Ps quenching rate constant by a Ps quencher.[4] In the two-component fitting analysis of the positron lifetime spectra, the first three components in (1) combine into one short-lifetime component and the fourth component in (1) becomes the long-lifetime component. Therefore

$$\lambda_2 = \lambda_p + \lambda_q \tag{2}$$

$$I_2 = \frac{3}{4} P \frac{\lambda - \lambda_p}{\lambda - (\lambda_p + \lambda_q)} \tag{3}$$

Since the Ps quenching by H^+ and Cl^- can be neglected[12] λ_q takes the form

$$\lambda_q = k_0[M] + k_p[MH^+] \tag{4}$$

where k_0 and k_p are the Ps reaction rate constants of free organic molecule and protonated one (−nium ion, MH^+), respectively. Therefore (2) is rewritten as

$$\lambda_2 = \lambda_p + k_0[M] + k_p[MH^+] \tag{5}$$

To express the Ps inhibition, we assume the following expression for the concentration dependence of Ps formation probability (P):[5,11]

$$P = \left(\frac{0.15}{1 + 60[Cl^-]} + 0.85\right) \times \left(\frac{1}{1 + 0.22[H^+] + \sigma_0[M] + \sigma_p[MH^+]}\right) \frac{4}{3} I_2^0 \tag{6}$$

Table I. The Best Fit Values of *o*-Ps Reaction Rate Constant k and Ps Inhibition Coefficient σ

compound	unprotonated		protonated	
	k_0, M^{-1} ns^{-1}	σ_0, M^{-1}	k_p, M^{-1} ns^{-1}	σ_p, M^{-1}
aniline	<0.01[a]	<1[a]	<0.01	<1
pyridine	<0.01	<1	0.08 ± 0.05	5.0 ± 0.4
pyrimidine	0.04 ± 0.03	1.7 ± 0.1	3.4 ± 0.3	8.2 ± 1.7
quinoline	0.05 ± 0.03[a]	1.1 ± 0.1[a]	4.4 ± 0.3	9.2 ± 1.3
quinoxaline	0.50 ± 0.05	4.8 ± 0.3	19 ± 1	20 ± 8

[a] In methanol solution.

where I_2^0 is the relative intensity of the long-lifetime component in the solvent and σ_0 and σ_p are the Ps inhibition coefficients of free organic molecule and protonated one, respectively. The term in the first parentheses and $0.22[H^+]$ in the second parentheses of (6) represent the weak Ps inhibition by Cl^- and H^+.[11,13] Combination of (3) and (6) yields

$$I_2 = I_2^0 \left(\frac{1}{1 + 0.22[H^+] + \sigma_0[M] + \sigma_p[MH^+]}\right) \times \left(\frac{0.15}{1 + 60[Cl^-]} + 0.85\right)\left(\frac{\lambda - \lambda_p}{\lambda - (\lambda_p + \lambda_q)}\right) \tag{7}$$

The concentration of the protonated organic ion $[MH^+]$ and that of the free organic molecule [M] can be calculated using the following equations:

$$\begin{matrix} M & + & H^+ & \rightleftarrows & MH^+ \\ (a - x) & & (\alpha a - x) & & (x) \end{matrix} \tag{8}$$

From the definition of the equilibrium constant K of the reaction (8), the following equality holds:

$$K = x/(a - x)(\alpha a - x) \tag{9}$$

x is the concentration of the protonated ion formed, a is the total concentration of organic molecule, and αa is the concentration of hydrogen ion added. Equation 9 can be solved for x as

$$x = \frac{a}{2}\left[(1 + \alpha) + \frac{1}{aK} - \left\{\left((1 + \alpha) + \frac{1}{aK}\right)^2 - 4\alpha\right\}^{1/2}\right] \tag{10}$$

(K = 20 for pyrimidine, K = 4.0 for quinoxaline, and $K = 7.9 \times 10^4$ for quinoline.)

Assuming $[Cl^-]$, $[H^+]$, and $[MH^+]$ = 0, the data obtained for the solutions containing only organic molecule were fitted to eq 5 and 7 (Figures 1-3). The values of k_0 and σ_0 giving best fits are given in Table I. These calculated values of k_0 and σ_0 were then introduced in (5) and (7). We could successfully fit the data obtained for the solutions containing both organic molecule and HCl to these equations with the k_p and σ_p values listed in Table I (Figures 1-3). The previous results of aniline and pyridine are also given in Table I.[9]

V. Discussion

Curves of Figures 1-3 indicate that the effect of concentration on λ_2 in quinoline, pyrimidine, quinoxaline-HCl systems depends mainly on the magnitude of the equilibrium constant K. For quinoline with $K = 7.9 \times 10^4$, the linear relationship is observed between λ_2 and the solute concentration. The relationship deviates from linearity with decreasing K as seen for pyrimidine (K = 20) and quinoxaline (K = 4.0). This trend is due to the fact that λ_2 is mainly dependent on the concentration $[MH^+]$, because $k_0 \ll k_p$ (eq 5). In principle it should be possible to determine the equilibrium constant K of the chemical reaction as in eq 8 from the positron lifetimes. The idea has already been demonstrated for the charge transfer complex formation reactions by several authors.[5,14]

The protonation of diazine, pyrimidine, or heteropolycyclic

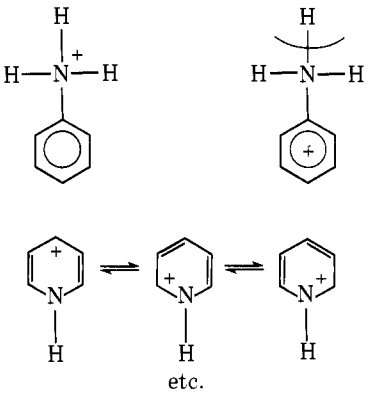
quinoline and quinoxaline enhances both the Ps reaction rate constant k and the Ps inhibition coefficient σ considerably as is shown in Table I. The protonation of pyridine, another heterocyclic molecule, enhances σ but not k and the protonation of aniline, which contains nitrogen but not a heteroring, gives almost no effect on both k and σ.

Extensive studies on the interaction of Ps with many diamagnetic molecules (temperature dependence of Ps quenching rate, study of solvent effect, etc.) by Gol'danskii et al.[2] and Ache et al.[3] revealed that the interaction is based on the following Ps complex formation:

$$M + Ps \rightleftharpoons [PsM] \quad (11)$$

Recently Schrader et al.[15] studied the stability of e^+ and Ps complexes of organic molecules by means of the semiempirical CNDO/2 method. Schrader's calculation on the ten benzene derivatives shows that the positron affinity does not change much from one molecule to another molecule (−0.35 to 0.52 eV). Therefore we expect that the Ps affinity, PsA, expressed as PsA = EA + PA^- − 6.8 eV, of a molecule is mainly determined by the electron affinity of the molecule, EA. (PA^- is the positron affinity of the electron-attached anion and 6.8 eV is the binding energy of Ps.)

The electron distribution or electron acceptability of the aniline molecule does not change much by protonation. Therefore anilinium ion is not likely to form stable complex with Ps. On the other hand, in the case of six-membered heterocyclic molecules such as pyridine, as shown below, electron density in the heteroring is reduced by protonation. This reduction of electron density would increase the electron acceptability and Ps affinity. Therefore the observed considerable enhancements of Ps reaction rate constants of pyrimidine, quinoline, and quinoxaline by protonation would be attributed to the Ps complex formation reaction.



$$MH^+ + Ps \rightleftharpoons [PsMH^+] \quad (12)$$

As one can see from Table I, pyrimidinium ion is a stronger Ps quencher than pyridinium ion, i.e., the ion which has two nitrogen atoms in the ring more strongly quenches Ps than the ion having one nitrogen. From the discussion given above, pyrimidinium ion or quinoxalinium ion is considered to be a stronger Ps acceptor than pyridinium ion or quinolinium ion. This consideration is reasonable because in the chemical species containing two nitrogens in the heteroring π electrons localize near the nitrogen atoms to a greater extent and the LUMO energy is lower than chemical species containing one nitrogen. The situation resembles the case of nitrobenzene and dinitrobenzene.

The experimental results presented here involve some problems to be solved (e.g., the specific inertness of pyridinium ion toward Ps, the difference of k's of the molecules containing different number of heterorings). After all, we think that a quantum mechanical approach for the stability of Ps complexes is required for the full understanding of the effect of protonation.

Problem of Ps Inhibition. At present, the following mechanisms have been proposed for the inhibition of Ps formation:[16-18] (1) capture of a positron by the solute molecule; (2) chemical reaction between a hot Ps and the solute molecule; (3) scavenging of electrons (dry or hydrated) in the positron spur by the solute molecule (spur reaction model).

As a reason for the increase of σ of heterocyclic molecules by protonation, mechanism (1) is ruled out, because the neutral molecule becomes the positive ion and should be less reactive toward the positron. Therefore the reason why σ of heterocyclic molecules increases by protonation is that it enhances the reactivity of the molecule toward the electron (spur model) or hot Ps (hot Ps theory).

Acknowledgment. The authors wish to express their thanks to K. Ueda and H. Nakagawa for constructing the positron lifetime spectrometer. We also would like to thank T. Ryuo for giving us the idea of this research and M. Onoda for helpful discussions and suggestions.

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