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Abstract

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DETERMINATION OF THE KINETIC CONSTANTS FOR THE INTERACTION OF POSITRONIUM WITH INORGANIC IONS

The experimental determination of rate constants for very fast chemical processes in a condensed phase is an important, but also difficult, problem of chemical kinetics in general and of radiation chemistry in particular.

Some new possibilities for determining such constants are opened up by experiments on the chemistry of positronium, since the values of the very short intrinsic lifetime of positronium (Ps) in vacuum can be used here as comparison standards: $1/\lambda_0 = 1.4 \cdot 10^{-7}$ sec for the triplet (ortho-) state and only $1.25 \cdot 10^{-10}$ sec for the singlet para-state.

The total rate constant for the destruction of ortho-positronium atoms in water, taking into account "pick-off" annihilation (1), is equal to:

$$\lambda_{\text{aq}} = \lambda_0 + K_{\text{pick-off}}[\mathrm{H_2O}] \simeq 6 \cdot 10^8\ \text{sec}^{-1}\ (^2).$$

The additional decrease in the reciprocal rate constant—the lifetime of ortho-positronium—upon dissolution in water of various additives, observed in (2), as well as the increase caused by such additives in the contribution of the narrow component of the angular distribution of annihilation γ-quanta (3), was interpreted as a consequence of ortho-para conversion of positronium $Ps^3 \rightarrow Ps^1$ on the unpaired electrons of the additives. However, along with conversion, various chemical reactions may also lead to a shortening of the lifetime of ortho-positronium in aqueous solutions in comparison with pure water; for example, oxidation by additives of Ps atoms with the formation of free positrons and their subsequent rapid annihilation (4–8). The total rate of destruction of ortho-positronium atoms in an aqueous solution with the addition of some acceptor (concentration [Ac]) is equal to:

$$-d[\mathrm{Ps}]/dt = \lambda_{\mathrm{aq}}[\mathrm{Ps}] + k[\mathrm{Ps}][\mathrm{Ac}] = [\mathrm{Ps}](\lambda_{\mathrm{aq}} + k[\mathrm{Ac}]), \qquad (1)$$

where k is the constant for the interaction of positronium with the acceptor. The experimentally determined annihilation rate constant in the presence of the acceptor is $\lambda = \lambda_{\mathrm{aq}} + k[\mathrm{Ac}]$, whence

$$k = (\lambda - \lambda_{\mathrm{aq}})/[\mathrm{Ac}]. \qquad (2)$$

In this case, the contribution of Ps oxidation, formation of a chemical bond with it, and positronium conversion to the constant K can be clarified by comparing the effects caused by ions of variable valence possessing different numbers of unpaired electrons.

Measurements of the Ps lifetime were carried out by us on an apparatus described earlier (^{5}), by recording delayed coincidences of annihilation γ-quanta and a nuclear cascade γ-quantum accompanying the positron, which gives the time mark for positron emission by a Na^{22} source. The results obtained (the average experimental error in determining the constants is ±30%) are given in Table 1, which also includes constants calculated from the data of (^{2})—for Cr^{3+}, Nd^{3+}, Co^{2+}.

Table 1

Acceptor	Conc., mol/l	Number of unpaired electrons	k, l/(mol·sec)	k_{av}, cm^3/sec	Acceptor	Conc., mol/l	Number of unpaired electrons	k, l/(mol·sec)	k_{av}, cm^3/sec
Substance strongly interacting with Ps with a decrease in τ_2					**Substance strongly interacting with Ps with a decrease in** τ_2				
Fe^{3+}	0.01	5	$1.1 \cdot 10^{10}$	$2 \cdot 10^{-11}$	$Cr_2O_7^{2-}$	0.005	0	$1 \cdot 10^{11}$	$1.5 \cdot 10^{-10}$

Acceptor	Conc., mol/l	Number of unpaired electrons	k, l/(mol·sec)	k_{av}, cm^3/sec	Acceptor	Conc., mol/l	Number of unpaired electrons	k, l/(mol·sec)	k_{av}, cm^3/sec
Fe^{3+}	0.03	5	$1.0 \cdot 10^{10}$	$2 \cdot 10^{-11}$	$Cr_2O_7^{2-}$	0.01	0	$0.8 \cdot 10^{11}$	$1.5 \cdot 10^{-10}$
Fe^{3+}	0.05	5	$1.4 \cdot 10^{10}$	$2 \cdot 10^{-11}$	$Cr_2O_7^{2-}$	0.015	0	$0.9 \cdot 10^{11}$	$1.5 \cdot 10^{-10}$
Cu^{2+}	0.02	1	$3.8 \cdot 10^{9}$	$7.5 \cdot 10^{-12}$	CrO_4^{2-}	0.03	0	$1 \cdot 10^{10}$	$1.5 \cdot 10^{-11}$
Cu^{2+}	0.06	1	$4.3 \cdot 10^{9}$	$7.5 \cdot 10^{-12}$	CrO_4^{2-}	0.06	0	$0.7 \cdot 10^{10}$	$1.5 \cdot 10^{-11}$
Cu^{2+}	0.2	1	$5.4 \cdot 10^{9}$	$7.5 \cdot 10^{-12}$	CrO_4^{2-}	0.3	0	$1 \cdot 10^{10}$	$1.5 \cdot 10^{-11}$
Ti^{4+}	0.05	0	$1.8 \cdot 10^{9}$	$3.3 \cdot 10^{-12}$	MnO_4^{-}	0.025	0	$0.9 \cdot 10^{10}$	$1.5 \cdot 10^{-11}$
Ti^{4+}	0.15	0	$2.2 \cdot 10^{9}$	$3.3 \cdot 10^{-12}$	MnO_4^{-}	0.05	0	$0.8 \cdot 10^{10}$	$1.5 \cdot 10^{-11}$
Ti^{4+}	0.40	0	$2.0 \cdot 10^{9}$	$3.3 \cdot 10^{-12}$	MnO_4^{-}	0.10	0	$1.0 \cdot 10^{10}$	$1.5 \cdot 10^{-11}$
UO_2^{2+}	0.01	0	$6.7 \cdot 10^{9}$	$1.2 \cdot 10^{-11}$	Fe^{2+}	0.1	4	$2.6 \cdot 10^{9}$	$3.5 \cdot 10^{-12}$
UO_2^{2+}	0.03	0	$7.7 \cdot 10^{9}$	$1.2 \cdot 10^{-11}$	Fe^{2+}	0.3	4	$1.9 \cdot 10^{9}$	$3.5 \cdot 10^{-12}$
UO_2^{2+}	0.1	0	$6.8 \cdot 10^{9}$	$1.2 \cdot 10^{-11}$	Fe^{2+}	0.5	4	$1.85 \cdot 10^{9}$	$3.5 \cdot 10^{-12}$
Ce^{4+}	0.03	0	$1.7 \cdot 10^{10}$	$2.8 \cdot 10^{-11}$	Mn^{2+}	0.2	5	$5.7 \cdot 10^{9}$	$1.1 \cdot 10^{-11}$
Ce^{4+}	0.10	0	$1.1 \cdot 10^{10}$	$2.8 \cdot 10^{-11}$	Mn^{2+}	0.6	5	$8.0 \cdot 10^{9}$	$1.1 \cdot 10^{-11}$
Ce^{4+}	0.3	0	$2.3 \cdot 10^{10}$	$2.8 \cdot 10^{-11}$	Mn^{2+}	1.0	5	$7.0 \cdot 10^{9}$	$1.1 \cdot 10^{-11}$
Sn^{4+}	0.025	0	$6.0 \cdot 10^{9}$	$0.9 \cdot 10^{-11}$	Ni^{2+}	0.07	2	$1.8 \cdot 10^{9}$	$2.75 \cdot 10^{-12}$
Sn^{4+}	0.05	0	$5.5 \cdot 10^{9}$	$0.9 \cdot 10^{-11}$	Ni^{2+}	0.15	2	$1.7 \cdot 10^{9}$	$2.75 \cdot 10^{-12}$
Sn^{4+}	0.10	0	$5.0 \cdot 10^{9}$	$0.9 \cdot 10^{-11}$	Ni^{2+}	0.30	2	$1.4 \cdot 10^{9}$	$2.75 \cdot 10^{-12}$
Cr^{3+}		3		$3.3 \cdot 10^{-12}$	Sn^{2+}	0.073	0	$0.9 \cdot 10^{9}$	$1.6 \cdot 10^{-12}$
Cr^{3+}		3		$3.3 \cdot 10^{-12}$	Sn^{2+}	0.20	0	$1.0 \cdot 10^{9}$	$1.6 \cdot 10^{-12}$
Cr^{3+}		3		$3.3 \cdot 10^{-12}$	Co^{2+}		3		3.3 · 10[[unclear:exponent]]

Acceptor	Conc., mol/l	Number of unpaired electrons	k, l/(mol· sec)	k_{av}, cm^3/sec	Acceptor	Conc., mol/l	Number of unpaired electrons	k, l/(mol· sec)	k_{av}, cm^3/sec
Substances having a small interaction constant with Ps					**Substances having a small interaction constant with Ps**				
U^{4+}	0.03	2	$< 10^7$	$< 10^{-14}$	H_2SO_4	0.01	0	$< 10^7$	$< 10^{-14}$
U^{4+}	0.10	2	$< 10^7$	$< 10^{-14}$	H_2SO_4	1.0	0	$< 10^7$	$< 10^{-14}$
U^{4+}	0.3	2	$< 10^7$	$< 10^{-14}$	H_2SO_4	1.0	0	$< 10^7$	$< 10^{-14}$
Ti^{3+}	0.05	1	$< 10^7$	$< 10^{-14}$	Na_2SO_4	0.05	0	$< 10^7$	$< 10^{-14}$
Ti^{3+}	0.15	1	$< 10^7$	$< 10^{-14}$	Na_2SO_4	0.2	0	$< 10^7$	$< 10^{-14}$
Ti^{3+}	0.40	1	$< 10^7$	$< 10^{-14}$	Na_2SO_4	1.0	0	$< 10^7$	$< 10^{-14}$
Ce^{3+}	0.03	1	$< 10^7$	$< 10^{-14}$	NaCl	0.1	0	$< 10^7$	$< 10^{-14}$
Ce^{3+}	0.10	1	$< 10^7$	$< 10^{-14}$	NaCl	0.5	0	$< 10^7$	$< 10^{-14}$
Ce^{3+}	0.3	1	$< 10^7$	$< 10^{-14}$	NaCl	1.0	0	$< 10^7$	$< 10^{-14}$
Pb^{2+}	0.25	0	$< 10^7$	$< 10^{-14}$					
Pb^{2+}	1.0	0	$< 10^7$	$< 10^{-14}$					
Nd^{3+}		3		$\sim 10^{-13}$					

The experimental data are presented in the table in two main groups: substances that interact strongly with Ps with a decrease in its lifetime, and substances with a small interaction constant. The first group is additionally divided into two subgroups—depending on the character of the effect of the additives on the form of the angular correlation of the annihilation γ-quanta*.

Substances whose interaction constants with atoms do not exceed 10^{-14} cm^3/sec include ions of lower and constant valence (for example, Na^+), hydrogen ions (hydroxonium). Changing the acidity of Fe^{2+} solutions from $5M$ H_2SO_4 to pH ~ 2, as well as additions of considerable amounts of Na_2SO_4, did not lead to a noticeable change in the rate constant of the reaction with Fe^{2+}, which confirms the negligibly small value, for these conditions, of the rate constant of the reaction of Ps with H^+ and Na^+. The smallness of the interaction constants for U^{4+}, Ti^{3+}, Ce^{3+}, Nd^{3+}, despite the presence of unpaired electrons in these ions, makes it possible to conclude that the contribution of "pure" conversion $Ps^3 \to Ps^1$ at the moment of collision to the processes of interaction of Ps with acceptors is very small.

For ions of higher valence this interaction has the character of oxidation of positronium—a process previously observed in works (3–8). In

* The angular-correlation experiments were carried out by B. G. Eghiazaryan.

This explanation is also supported by the fact that the ions Ti^{4+}, UO_2^{2+}, Ce^{4+}, Sn^{4+}, $Cr_2O_7^{2-}$, CrO_4^{2-}, MnO_4^- rapidly enter into reaction with Ps atoms, despite their diamagnetism and the absence of unpaired electrons. The interaction constants for them are so large that they compel one to assume the possibility that even singlet positronium enters into a chemical reaction. A confirmation of the oxidative interaction is also provided by the broadening of the angular-correlation curves of annihilation γ quanta for ions of this subgroup. We note, finally, that quenching of positronium by Fe^{3+} and Sn^{4+} ions is much stronger than for Fe^{2+} and Sn^{2+}.

Ions of the other subgroup are also characterized by a rather high rate of interaction with Ps atoms, irrespective of the presence (Fe^{2+}, Mn^{2+}, Ni^{2+}, Co^{2+}) or absence (Sn^{2+}) of unpaired electrons. However, in these cases, when unpaired electrons are present, no broadening of the angular-correlation curves is observed; on the contrary, there is an enhancement of the narrow component, indicating a definite influence of ortho-para conversion. The formation, upon interaction of Ps with ions of this subgroup, of ions of still lower valence is highly unlikely on energetic grounds. Here it is more natural to assume the reduction of Ps to Ps^- or the formation of compounds of the hydride type (positronides), with possible subsequent internal conversion $^3S \to {}^1S$.

Table 2

Acceptor	$K_{\mathrm{Ac+H}}$	$K_{\mathrm{Ac+Ps}}$	E_{H}, kcal/mol	p
Fe++	$6.7 \cdot 10^5$	$2 \cdot 10^9$	4600	$1.5 \cdot 10^{-3}$
Fe+++	$4.8 \cdot 10^6$	$1.2 \cdot 10^{10}$	4400	$9 \cdot 10^{-3}$

Since positronium, in its chemical behavior, is a direct analogue of the hydrogen atom, it is of interest to compare the rate constants of reactions involving hydrogen atoms and positronium. An example of such a comparison is given in Table 2.

The total values of $K_{\mathrm{Ac+H}}$ (in liters/mol • sec) are taken from work (^{9}); $K_{\mathrm{Ac+Ps}}$ was obtained in the present work; the calculation of the activation energy E_{H} of the reactions of acceptors with hydrogen and of the steric factors p is explained below. It is evident that the rate constants $K_{\mathrm{Ac+Ps}}$ exceed $K_{\mathrm{Ac+H}}$ by more than three orders of magnitude.

In principle, two approaches are possible to explain this acceleration of reactions involving Ps in comparison with H.

The first variant reduces to the assumption of the formation of an intermediate complex H—Ac or Ps—Ac, requiring a certain activation energy because of the presence of solvation shells around the acceptor ion.

The existence of such a complex is assumed, in particular, in the reaction H + $\mathrm{Fe}^{\cdot\cdot}$, which proceeds, according to (^{10}), in two stages: $\mathrm{H} + \mathrm{Fe}^{\cdot\cdot} \to \mathrm{HFe}^{\cdot\cdot}$ and $\mathrm{HFe}^{\cdot\cdot} + \mathrm{H}^{\cdot} \to \mathrm{H}_2 + \mathrm{Fe}^{\cdot\cdot}$, of which the first is rate-limiting.

The second variant requires a consistent quantum-mechanical consideration of the spatial distribution of the wave functions forming the positronium atom—electron and positron. We note, in particular, that a sub-barrier transition of an electron from the positronium atom to the acceptor may prove more probable than the transition from a hydrogen atom, since in the case of positronium the resonance conditions of the electron levels in the initial and final states should be less stringent, because the positron, as a light and penetrating particle, can effectively absorb the recoil energy associated with the difference in the positions of the levels.

The subsequent consideration is based on the first of the variants named; moreover, it is assumed that the acceleration of reactions involving Ps is associated with its penetration as a whole through the activation barrier owing to its small mass. Thus, under conditions in which, for hydrogen atoms, the contribution of tunneling transitions exponentially predominates over the Arrhenius contribution only at $T < 50°\mathrm{K}$, for positronium atoms the tunneling effect begins to play a decisive role already at $T < 1600°\mathrm{K}$ (^{11}).

Let us write the general expression for the rate constant in the form:

$$K = p\pi(r_1+r_2)^2\sqrt{\frac{8kT}{\pi\mu}}\left[\left(\frac{E}{RT}\right)^2\left\{\int_0^1 y\omega(y)e^{-yE/RT}\,dy + \int_1^\infty ye^{-yE/RT}\,dy\right\}\right], \tag{3}$$

where p is the steric factor, $\omega(y)$ is the probability of a tunnel transition, y is the dimensionless energy in fractions of the activation energy E, and all other quantities are generally known.

For $\omega(y) = 0$, we obtain for the reaction $\mathrm{Ac} + \mathrm{H}$

$$K_{\mathrm{Ac+H}} = p\pi(r_H + r_{\mathrm{Ac}})^2 \sqrt{\frac{8kT}{\pi\mu}} \left(1 + \frac{E_H}{RT}\right) e^{-E_H/RT}; \tag{4}$$

for $\omega(y) = 1$ the term in square brackets becomes unity and the rate constant contains only the pre-exponential factor.

The positronium case may be close to this; thus, for a parabolic barrier of width 2 Å, at $E/RT = 8$ and $T = 300^\circ$K, from (3) we obtain

$$K_{\mathrm{Ac+Ps}} = p\pi(r_{\mathrm{Ps}} + r_{\mathrm{Ac}})^2 \sqrt{8kT/\pi\mu} \cdot 0.22 \tag{5}$$

(we assume that the positronium atoms are characterized by a Maxwellian distribution; for a geometrical cross section of elastic collisions of positronium atoms with water molecules, the thermalization time is close to $3 \cdot 10^{-11}$ sec.)

Comparing now (4) and (5), and taking into account that

$$\frac{\mu_{\mathrm{Ps}}}{\mu_H} = \frac{1}{920}; \qquad \left(\frac{r_{\mathrm{Ps}} + r_{\mathrm{Ac}}}{r_H + r_{\mathrm{Ac}}}\right)^2 \simeq 1.8,$$

we obtain

$$\frac{K_{\mathrm{Ps+Ac}}}{K_{\mathrm{H+Ac}}} = \frac{12 e^{E_H/RT}}{1 + E_H/RT},$$

whence the values of E_H and of the steric factors p (taken to be the same for H and Ps) given in Table 2 are calculated.

In conclusion, let us note that under the conditions of our experiments no change in the lifetime of positronium was observed with change in the pH value of aqueous solutions, i.e., the rate constant of the reaction $\mathrm{Ps} + \mathrm{H}^+$ was less than 10^{-14} cm^3/sec, which corresponds to the sensitivity limit of our apparatus. If in this case as well the activation energy of the corresponding reaction of H atoms is close to the values given in Table 2, then the rate constant of the reaction $\mathrm{H} + \mathrm{H}^+$ in aqueous solutions should not exceed approximately $3 \cdot 10^{-18}$ cm^3/sec, which is confirmed by the values $K_{\mathrm{H+H^+}} \simeq 10^{-18}$–$10^{-17}$ cm^3/sec reported in ([12–14]).

The data presented indicate the possibility of applying studies of positron annihilation to the determination of kinetic constants of fast processes in the condensed phase, and perhaps also the possibility of obtaining in this way additional information on the role of tunnel transitions in chemical reactions. To obtain such information, studies of the temperature dependence of the rate constants of chemical reactions involving positronium appear especially interesting.

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