AIP | The Journal of Chemical Physics

Mean Lives of Positrons in Aqueous Solutions

Jerome E. Jackson and John D. McGervey

Citation: The Journal of Chemical Physics **38**, 300 (1963); doi: 10.1063/1.1733655
View online: http://dx.doi.org/10.1063/1.1733655
View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/38/2?ver=pdfcov
Published by the AIP Publishing

THE JOURNAL OF CHEMICAL PHYSICS VOLUME 38, NUMBER 2 15 JANUARY 1963

Mean Lives of Positrons in Aqueous Solutions*

JEROME E. JACKSON AND JOHN D. MCGERVEY
Western Reserve University, Cleveland, Ohio
(Received 10 September 1962)

By measurement of the time distribution of positron annihilations in aqueous solutions, reaction rates for oxidation of positronium by the ions MnO_4^-, IO_3^-, and Hg^{++} have been determined. In strong oxidizing solutions the mean life of the positrons reaches a lower limit of 4.3×10^{-10} sec; the short lifetime τ_1 in water was measured and found to agree with this value. A $Pb(ClO_4)_2\cdot 3H_2O$ solution reduced the intensity I_2 with no significant change in the long life τ_2, an effect previously observed in nitrate solutions. This may mean that in these two cases oxidation can occur before Ps is thermalized but not afterwards. The decay distributions from a mixture of Hg^{++} and MnO_4^- ions in solution and the Hg^{++} ion in separate solutions with Cl^- and ClO_4^- indicated an association taking place between the negative and positive ions.

INTRODUCTION

THE study of positron annihilations in liquids is directed toward understanding the type of interaction that leads to the formation or destruction of bound states prior to annihilation. In water approximately $\frac{1}{3}$ of the positrons pair with an electron through an electrostatic attraction forming a hydrogen-like system called positronium (Ps). This system is considered stable even though the electron and positron annihilate in a short time. Conditions are favorable for Ps formation when the positrons entering water are slowed by inelastic collisions to an energy that lies in the range called the "Ore gap." For the positron to be within the Ore gap its energy must be less than the first excitation potential of the surrounding molecules, but not below the first ionization potential minus the binding energy of Ps ($E_e \geq KE \geq E_i - E_b$).

The paired electron and positron in positronium may form a singlet (spins antiparallel) or triplet (spins parallel) state. The mean life for the singlet state is 1.25×10^{-10} sec, decaying by self-annihilation. The triplet state lives much longer, 1.4×10^{-7} sec, thus allowing other decay mechanisms to take place before self-annihilation.

The formation of Ps in water was demonstrated by the positron lifetime measurements of Bell and Graham.[1] Later Green and Bell found a complex decay with about 20% of the positrons having a long mean life, $\tau_2=1.8\times10^{-9}$ sec, and the rest having a mean life of about 3×10^{-10} sec.[2] The positrons with the short mean life arise from singlet Ps and from positrons which reach thermal energy without capturing an electron, and annihilate as free positrons. Those with the long mean life form triplet Ps and are partially shielded from the surrounding electrons, but eventually decay by annihilations with neighboring electrons by the "pickoff" process.[3]

The existence of an atom of Ps in water enables one to study chemical reactions between it and ions in solution. When good oxidizing agents are added to water, the ions formed capture the electron from the Ps atom. This leaves the positron with an energy too low to form another Ps atom. Without its paired electron the positron is no longer shielded from other electrons, thus its mean life in water is shortened. This effect on the mean life has been previously observed for the ions Hg^{2+}, Sn^{4+}, and Sb^{3+}.[4] Measurements of the angular correlation of the two annihilation gamma rays also indicated the oxidation of Ps by the ions Cu^{2+} and MnO_4^-.[5]

In a collision the Ps atom may be destroyed by oxidation if the electron energy level of the resulting product ion is lower than it was in Ps. Even when the electron energy level for Ps is lower than the product ion, the transfer of an electron may still be possible if the lacking energy is supplied by the kinetic energy of the reactants. The lower the product ion energy level the better it performs as an oxidizing agent; the corresponding oxidation potential is chosen here to become more positive and is given in Table I in this sense. The oxidation potentials only partially reflect the ability of these ions to act as oxidizing agents of Ps. The value for an ion's oxidation potential is obtained in many cases from a cell reaction involving several electrons, whereas when this ion reacts with Ps, only one electron is transferred. An example of what may happen is given by the IO_3^- ion in Table I; its oxidation potential was determined from a cell reaction involving six electrons. It is seen that the IO_3^- ion has a higher oxidation potential than the Hg^{2+} and MnO_4^- ions, but is the least effective as an oxidizing agent.

The reaction between Ps and an oxidizing ion is different in another way from the usual oxidation–reduction process; the Ps reaction does not come to equilibrium. The reverse reaction involving the reduction of Ps does not take place because the Ps ion, a positron, decays almost immediately. Without equilibrium, definite limits cannot be assigned to the oxida-

* Research supported in part by the U. S. Air Force Office of Scientific Research.

[1] R. E. Bell and R. L. Graham, Phys. Rev. **85**, 644 (1953).
[2] R. E. Green and R. E. Bell, Can. J. Phys. **35**, 398 (1957).
[3] R. E. Green and R. E. Bell, Can. J. Phys. **36**, 1684 (1958).
[4] J. D. McGervey, H. Horstman, and S. DeBenedetti, Phys. Rev. **124**, 1113 (1961).
[5] G. Trumpy, Phys. Rev. **118**, 688 (1960).

TABLE I. Mean lives of positrons in aqueous solutions, in millimicroseconds.

Solution	Oxidation potential	Concentration in moles per liter 1/256	1/128	1/64	1/32	1/16	1/8	1/4	1/2	1	2
$KMnO_4$	0.58	1.57±0.07	1.25±0.10	1.02±0.05	0.75±0.04	0.45±0.04	0.41±0.04				
$HgCl_2$	0.92		1.51±0.04[a]	1.40±0.04[a]	1.14±0.08	0.94±0.10	0.58±0.05	0.45±0.05			
KIO_3	1.192					1.77±0.10	1.47±0.05				
$Pb(ClO_4)_2 \cdot 3H_2O$	−0.126									1.75±0.10	1.74±0.04
$Hg(ClO_4)_2 \cdot 9H_2O$	0.92						1.17±0.13				
Mixture (1/32 *M* $KMnO_4$ +1/16 *M* $HgCl_2$)					0.88±0.03						

[a] See reference 4.

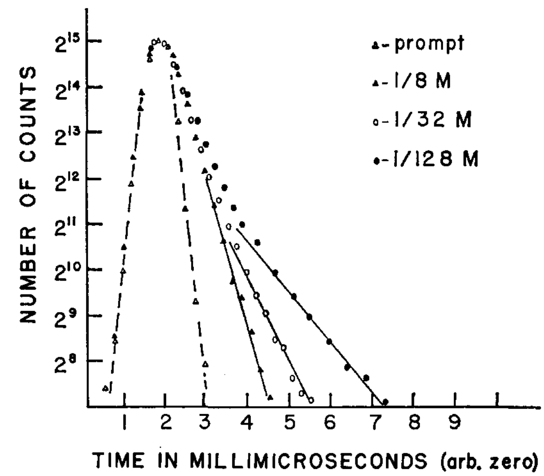

FIG. 1. Time distribution of positron annihilations in aqueous solutions of $KMnO_4$. The prompt curve was obtained from the gamma rays of Co^{60}.

tion potential or binding energy of Ps in solution.[4] The decay distributions of positrons in these solutions where chemical reactions take place do give definite information. The observed lifetime of Ps provides a direct measurement of the forward reaction rate of Ps with an oxidizing ion.

EXPERIMENTAL PROCEDURE

A 5-μCi source of Na^{22} in the form of NaCl dissolved in HCl was evaporated to dryness in a glass vial, 1 cm in diam and 3 cm high. The solution studied was then deposited in the vial and sealed. With this arrangement less than 2% of the positrons annihilated in the glass. Na^{22} emits almost simultaneously a positron and a 1.3-MeV gamma ray; the positron annihilates in the solution giving off two 0.511-MeV gamma rays. The apparatus measures the time interval between the nuclear gamma ray and one of the annihilation gamma rays.

Details of short lifetime measurements are well known. Two scintillation counters view the radiation; a pulse from one dynode of each counter goes to an amplifier and pulse height selector which selects a 1.3-MeV gamma ray from one counter and a 0.511-MeV annihilation gamma ray from the other. When the two selector outputs are in coincidence, a gate is opened allowing a 60-channel pulse-height analyzer to accept and sort a pulse from a time-to-amplitude converter. The converter output is proportional to the time difference between fast pulses in the two counters. Measured delay cables inserted between the counter and converter inputs establish the time scale by shifting the peak of the distribution a given amount. This calibration was linear to within 2% and remained stable to within 2% over periods of several days. A "prompt" curve, obtained by using the gamma rays of Co^{60} (see Fig. 1), has a width at half maximum of 0.75×10^{-9} sec.

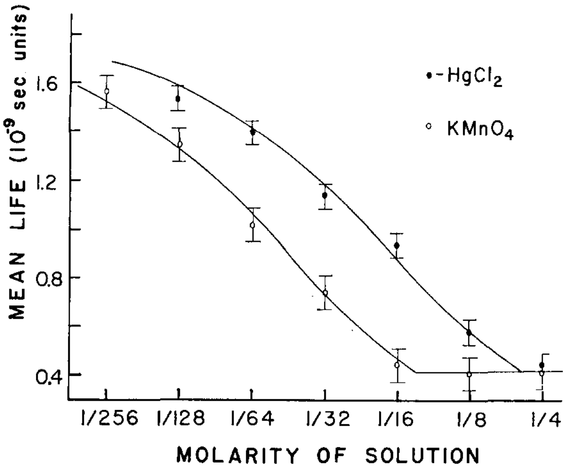

FIG. 2. Variation of positron mean lives with concentration of the oxidizing solution. The experimental points fit the solid curve, which was drawn under the assumption that the oxidation rate is proportional to concentration.

After approximately a 10-h run a distribution of positron lifetimes was obtained. The right-hand slope of the distribution gives the mean life of the positrons in a particular liquid environment.

RESULTS AND DISCUSSION

Considering just the two major processes, pickoff and oxidation, the total annihilation probability was found to be the sum of the probabilities for each decay mechanism. For sufficiently long times the observed decay constant λ_t is $\lambda_t = \lambda_0 + \lambda_p$ if $\lambda_0 + \lambda_p \leq \lambda_f$ or $\lambda_t = \lambda_f$ if $\lambda_0 + \lambda_p \geq \lambda_f$, where λ_0 is the oxidation probability per unit time, λ_p is the pickoff annihilation probability, and λ_f is the free positron annihilation probability per unit time.[4]

The time distribution of positron decay in the aqueous solutions of $KMnO_4$, $HgCl_2$, and KIO_3 clearly shows an exponential decay that is the result of oxidation taking place. Two effects serve as evidence that Ps is really oxidized. First, the amount of the oxidizing agent added to shorten the mean life from water by a given amount is related to the oxidation potential of the negative or positive ion in question (MnO_4^-, Hg^{2+}, IO_3^-). Second, the variation of positron mean life with different concentrations of these solutions indicates that λ_0 is proportional to concentration; this proportionality is shown in Fig. 1 for a $KMnO_4$ solution. In Fig. 2 the mean life of the positron was plotted as a function of concentration; the solid curve was drawn under the assumption that λ_0 is proportional to concentration. The observed mean life $1/(\lambda_0+\lambda_p)$ was calculated as a function of λ_0 by letting λ_0 vary by factors of two in "units" of λ_p, corresponding to similar changes in concentration. The experimental points provide a good fit to the calculated curve.

In the region of high concentrations Fig. 2 also shows that the curves for $KMnO_4$ and $HgCl_2$ reach a constant value; this value is almost the same for both solutions and equals approximately 4.3×10^{-10} sec. At these concentrations, where the condition $\lambda_0+\lambda_p \geq \lambda_f$ is fulfilled, a constant mean life is expected, namely $1/\lambda_f$. In the limit of high concentrations the oxidizing ions destroy Ps as quickly as it is formed, leaving all the positrons free in water with a constant probability of decay.

The picture presented above would be verified if it could be shown that the value of the lower limit of τ_2 is identical to the mean life of free positrons in solution. But a separate determination of $1/\lambda_f$ can be made from the complex decay of positrons in pure water. The density of a $\frac{1}{4}M$ solution of $KMnO_4$ is only 4% greater than water and is therefore similar to water, as far as free thermalized positrons are concerned. The slope of the long exponential in water, determined by the decay of triplet Ps through the pickoff process, was extrapolated to $t=0$ and subtracted from the total counts to obtain the short lived component (Fig. 3). The short mean life τ_1 comes from the annihilation of free positrons in water. The mean life calculated in this way was $(4.2\pm0.2)\times10^{-10}$ sec. The close agreement between τ_1 and the limiting mean life verifies that an oxidation process reduces the mean life in these solutions.

The earlier result of 3×10^{-10} sec obtained by Bell and Graham using the "centroid shift" method does not agree with this value. Gerholm pointed out, however, that an error of the order of 10^{-10} sec from the instrumentation alone was possible in their results.[6]

Considering the complex nature of solutions, it is surprising that the explanation of the above data could be given in terms of just two processes, oxidation and

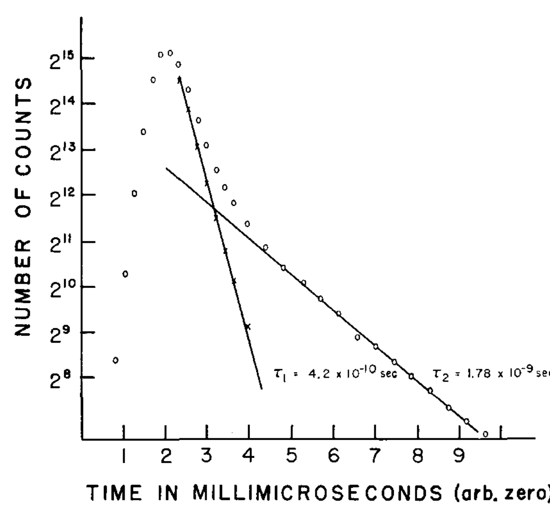

FIG. 3. Complex decay distribution of positrons in H_2O; subtracting the extrapolated component gives the short mean life for free positrons.

[6] T. R. Gerholm, Arkiv Fysik **10**, 523 (1956).

pickoff, and that λ_0 is simply proportional to concentration. To pursue the validity of these assumptions further, the solutions $Hg(ClO_4)_2 \cdot 9H_2O$ and $HgCl_2$ were studied. The negative ions Cl^- and ClO_4^- produce no oxidation; solutions with the Cl^- ion have been studied previously,[4] and the solutions $Ba(ClO_4)_2$ and $Li(ClO_4)$, studied in this work, gave similar results of causing no oxidation. The $\frac{1}{8}M$ solution of $Hg(ClO_4)_2 \cdot 9H_2O$ reduced the τ_2 component by oxidation, but by an amount less than the Hg^{2+} ion in a $\frac{1}{8}M$ solution of $HgCl_2$. This seems to indicate a greater association between the ClO_4^- and Hg^{2+} ions, which reduces the ability of Hg^{2+} to oxidize Ps. There is supporting evidence for this reasoning from chemical data which gives the ClO_4^- ion a larger association constant than Cl^-.

Another test of the association effect was made by mixing a $\frac{1}{16}M$ solution of $HgCl_2$ with a $\frac{1}{32}M$ solution of $KMnO_4$. The observed mean life for positrons was greater than in the pure $KMnO_4$, indicating some type of association which greatly reduced the oxidizing power of both the Hg^{2+} and MnO_4^- ions.

The intensity of the long-lived component is a measure of the number of positrons that form thermalized triplet Ps. The intensity was taken as the percentage of true counts in the long lived exponential to the total number of counts in the entire distribution. In water and poor oxidizing solutions that cause no significant decrease in τ_2, the intensity was $21 \pm 5\%$. A $2M$ solution of $Pb/(ClO_4)_2 \cdot 3H_2O$ produced an unexpected decrease in the intensity, as shown in Fig. 4. A similar result was obtained for $NaNO_3$ by Green and Bell; a large reduction in intensity was observed with no significant change in the long lifetime itself.[2] This effect was explained by assuming that many of the free positrons are captured by the NO_3^- ion forming a stable compound. The new "molecule" then decays at a rate comparable to singlet Ps, thus reducing the intensity. This is somewhat unsatisfactory in view of the fact that six other monovalent negative ions (Cl^-, ClO_3^-, ClO_4^-, BrO_3^-, IO_3^-, and MnO_4^-) cause no change in intensity. The absence of this effect in other ClO_4^- solutions indicates that the effect in $Pb(ClO_4)_2 \cdot 3H_2O$ is caused by the Pb^{++} ion, so that the positron capture idea is inapplicable to this case.

Giving a detailed picture of the Ore gap in a complex liquid medium would be difficult, but a closer consideration of the energy available for Ps formation might still prove useful for explaining the above effect. The Ps atom may be formed with a kinetic energy of up to 2 eV, 100 times greater than its thermal energy. Even though the thermalization time is approximately 10^{-10} sec, one would expect that with this added kinetic energy the Ps atom could be oxidized by an agent whose electron affinity in solution is equal to or less than the Ps atom. Since in the experiment the radiation is viewed at times long compared to the thermalization time, this effect would just appear as a decrease in the intensity of the long lived component. The conclusion is that the Pb^{++} and NO_3^- ions can oxidize Ps before it is thermalized, but not afterwards.

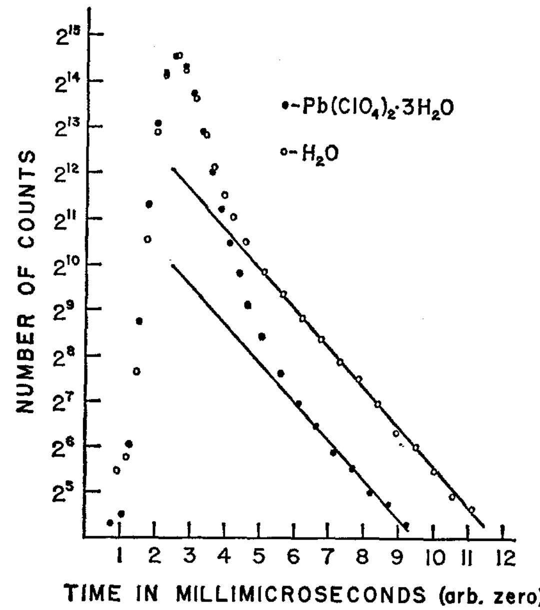

FIG. 4. Time distribution of positron annihilations in an aqueous solution of $Pb(ClO_4)_2 \cdot 3H_2O$. The H_2O distribution is used for the purpose of comparison.

The speed of the reaction between Ps atoms and both negative and positive ions has been measured directly. This speed was not only related to the oxidation potential of the ions, but also to the degree of association occurring in the solution. Future studies involving both lifetime and intensity measurements may help to give more information on the nature of chemical bonds in solution.