

Mean Lives of Positrons in Oxidizing Solutions*

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Mean lives of positrons have been measured in aqueous chloride solutions, in an attempt to detect oxidation of positronium (Ps) by positive ions. The variation of mean life with concentration and with oxidation potential of the positive ion shows that Ps is oxidized by solutions of SnCl_4 and HgCl_2 , but not by HCl or solutions of ions with lower oxidation potentials. These results indicate that the process is quite similar to the ordinary chemical oxidation process.

INTRODUCTION

SINCE the detection by Bell and Graham¹ of the formation of positronium (Ps) in water, positrons have been used as a probe to observe ionic processes in solutions. The fate of a positron in an aqueous solution is summarized in the flow chart in Fig. 1.

Fast positrons entering water are slowed by inelastic collisions until their remaining energy may be in the range called the "Ore gap," in which Ps formation is the only possible result of an inelastic collision. But if a positron's last inelastic collision reduces its energy from a value above the "Ore gap" to a value below that required to capture an electron, it will lose further energy by elastic collisions only and will annihilate as a free positron, with a mean life of a few times 10^{-10} sec in water. The experimental evidence on positron lifetimes indicates that the determination whether or not Ps is formed must occur very shortly after the positron's creation, in a time of the order of 10^{-11} sec.

Three fourths of the Ps formed is in the triplet state, and one fourth is in the singlet state. But the mean life of triplet Ps is 1.4×10^{-7} sec, compared to only 1.25×10^{-10} sec for singlet Ps. Thus the singlet Ps decays mostly by self annihilation, while the triplet Ps decays by annihilation with an electron "picked off" from the surrounding medium. In pure water, the mean life for this last process is 1.8×10^{-9} sec.

The measurement of this long mean life furnished proof of the formation of Ps in water.¹ The presence of singlet Ps has also been detected by angular correlation measurements of the annihilation gamma rays: When a thermalized singlet Ps atom annihilates, the momentum of the annihilating pair is smaller than it is when a thermal positron annihilates with an electron from the surrounding medium, as in the case of either free positron or pickoff annihilation. This smaller momentum is detected as a "narrow component" in the angular distribution of the gamma rays: More pairs of gamma rays are emitted at angles close to 180° .²

The flow chart indicates the observable effects of the introduction of various kinds of ions into the water.

Paramagnetic ions, in which there are one or more electrons with unpaired spins, may exchange an electron with the Ps atom and thus convert it from triplet to singlet or vice versa. The effects of this exchange are to shorten the long mean life and to increase the number of singlet annihilations from bound Ps, thus increasing the number of counts observed in the narrow component in an angular correlation measurement. In the limit of an infinitely rapid conversion rate and in the absence of other processes of annihilation, the mean life would be equal to four times the singlet mean life, or 5×10^{-10} sec, since the Ps would spend one fourth of its time in the singlet state. The presence of the pickoff mechanism reduces this limit to 3.9×10^{-10} sec, which has been observed by Green and Bell.³

The presence of ions which are good oxidizing agents may produce another effect. These ions may simply capture the electron from the Ps atom, just as they do when they oxidize ordinary elements. This would leave a bare positron which would probably have insufficient energy to form a new Ps atom and would therefore have a shorter life expectancy than it had before. Thus oxidation would reduce the mean life, just as the conversion process does; but since some singlet Ps is also destroyed in the process, the number of counts in the narrow angular component would be reduced instead of increased as it is by the conversion process. Oxidation would also cause a decrease in the three-quantum annihilation rate; attempts to detect oxidation by observing this decrease have been reported in a previous paper.⁴

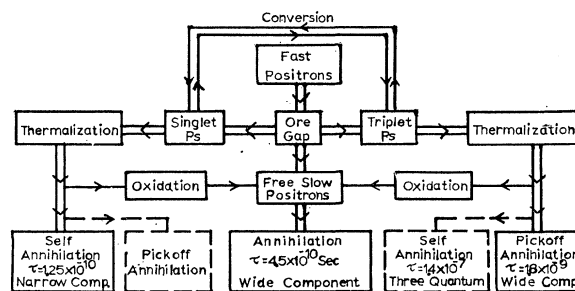


FIG. 1. Flow chart showing the possible reactions of positrons in aqueous solutions.

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¹ R. E. Bell and R. L. Graham, *Phys. Rev.* **90**, 644 (1953).

² R. L. deZafra and W. T. Joyner, *Phys. Rev.* **112**, 19 (1958).

³ R. E. Green and R. E. Bell, *Can. J. Phys.* **36**, 1684 (1958).

⁴ J. McGervey and S. DeBenedetti, *Phys. Rev.* **114**, 495 (1959).

More recently Trumpy has observed a decrease in the narrow component of the annihilation radiation from CuCl_2 solutions.⁵ Since CuCl_2 is paramagnetic, one would expect an increase in this component, as observed in other paramagnetic salt solutions. The decrease actually observed indicates that the Cu^{++} ion oxidizes Ps, and that the decrease in the number of singlet annihilations, caused by oxidation, is greater than the increase caused by conversion.

The purpose of this paper is to report a systematic study of mean lives of positrons in chloride solutions, as a function of oxidation potential and concentration of the positive ion. It has been established that oxidation of Ps occurs in just those solutions which are good oxidizers in ordinary chemical processes, and the speed of oxidation has been determined in these solutions.

APPARATUS AND PROCEDURE

About 5 microcuries of Na^{22}Cl were dissolved directly into each of the aqueous solutions to be studied; the solutions were sealed in glass vials, 1 cm in diameter and 3 cm high. This insured that less than 2% of the positrons emitted by the Na^{22} would annihilate in the walls of the container.

The procedure for measuring the mean lives has become fairly standardized. The nucleus used sets the zero of the time scale; after emission of the positron, the remaining nucleus is an excited state of Ne^{22} , which decays within 10^{-14} sec by emission of a 1.3-Mev gamma ray. One scintillation counter detects this gamma ray; a second counter detects the annihilation gamma ray. A time-to-amplitude converter⁶ puts out a pulse whose amplitude is proportional to the time

difference between pulses in these two counters. This output is gated by pulse-height selectors in coincidence to insure that the pulse in one counter originates from the 1.3-Mev gamma ray and the pulse in the other counter comes from the 0.51-Mev annihilation gamma ray. The gated output is then fed to a multichannel analyzer which records the number of pulses in each amplitude range. The correlation between amplitude and time is made by delaying the pulse from one counter by means of measured cables and observing the resulting change in pulse height in the output of the converter.

RESULTS

Figure 2 shows the time distribution of positron annihilations in HgCl_2 solutions of different concentrations. Each curve shows an exponential decay starting at about 3 nsec after the creation of the positron. The reciprocal of the decay constant is the observed mean life of the positrons which have formed Ps.

In Table I are shown the mean lives which have been determined in this manner for positrons in various chloride solutions. The positive ions are listed in order of oxidizing power, as roughly indicated by the oxidation potential. (The oxidation potentials listed in the table are for the reaction which seems most appropriate to this system; this will be discussed further in the next section.)

Table I shows that the positive ions with oxidation potentials of +0.13 or more all have a large effect on the mean life, even at relatively small concentrations, while those of oxidation potential 0.00 or less all have a small effect. The reduction in mean life which is observed in some of the latter solutions may be attributed to the effect of density, which for high concentrations may be considerably larger than the density of pure water. For example, a two molar solution of AlCl_3 has a density of 1.18, and one would expect a greater pickoff annihilation rate than in pure water; the observed reduction of about 10% in positron mean lives could be due to this effect.

The large effects observed only in solutions of SnCl_4 , SbCl_3 , and HgCl_2 , and the fact that the effect increases monotonically with increasing oxidation potential are strong evidence that Ps is oxidized in these solutions. More evidence is provided by the way in which the mean life varies with concentration. If oxidation is the process responsible for shortening the mean life, the dependence of the observed mean life on concentration may be calculated as follows: Since the time, t , is always measured from the creation of a positron, the situation is exactly as if at some initial time, $t=0$, a certain number, N_0 , of triplet Ps atoms were present. The free positrons and singlet Ps atoms present at $t=0$ may be ignored, since at the time of observation t was much greater than $1/\lambda_f$, where λ_f is the free positron annihilation probability per unit time. At time t the number of Ps atoms present is N_p and the number of free positrons (from

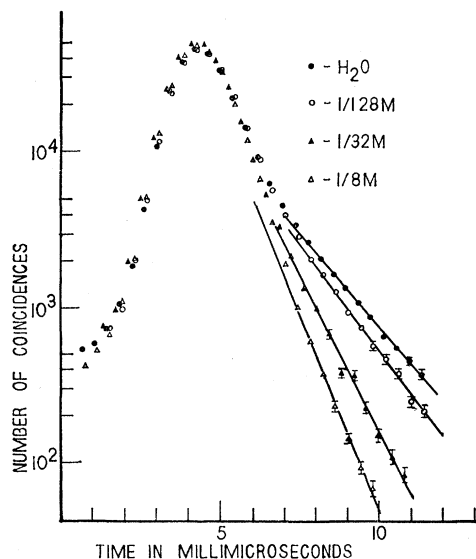


FIG. 2. Time distribution of positron annihilations in aqueous solutions of HgCl_2 .

⁵ G. Trumpy, Phys. Rev. 118, 668 (1960).

⁶ J. V. Kane (private communication).

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

Solute	Oxidation potential	Concentration, in moles per liter								
		1/128	1/64	1/32	1/16	1/8	1/4	1/2	1	2
KCl	−2.92									1.69±0.07
AlCl ₃	−1.70									1.61±0.10
CdCl ₂	−0.40							1.59±0.10	1.56±0.08	1.49±0.07
SnCl ₂	−0.13							1.51±0.10		1.42±0.10
HCl	0.00									1.75±0.07
SnCl ₄	+0.13				1.65±0.10	1.52±0.10	1.20±0.10	1.00±0.10	0.70±0.10	
SbCl ₃ ^a	+0.21			1.76±0.10	1.68±0.10	1.36±0.10	1.00±0.07			
HgCl ₂	+0.92	1.51±0.04	1.40±0.04	1.09±0.04	0.94±0.04	0.65±0.04				

^a Values for SbCl₃ were measured by R. E. Green and R. E. Bell, Can. J. Phys. 36, 1684 (1958).

oxidized Ps) is N_f . The oxidation probability per unit time is λ_0 and the pickoff annihilation probability is λ_p . Then if the self-annihilation probability of triplet Ps is ignored, the numbers N_p and N_f obey the equations

$$dN_f/dt = -\lambda_f N_f + \lambda_0 N_p, \quad (1)$$

$$dN_p/dt = -\lambda_p N_p - \lambda_0 N_p. \quad (2)$$

The solution of these equations, with $N_p = N_0$ and $N_f = 0$ at $t = 0$, is

$$N_p = N_0 \exp[-(\lambda_0 + \lambda_p)t], \quad (3)$$

$$N_f = \frac{\lambda_0 N_0}{\lambda_f - (\lambda_0 + \lambda_p)} \{ \exp[-(\lambda_0 + \lambda_p)t] - \exp(-\lambda_f t) \}. \quad (4)$$

The total number of positrons present thus exhibit two decay constants, λ_f and $\lambda_0 + \lambda_p$. For sufficiently large t , the observed decay constant λ_t will be

$$\begin{aligned} \lambda_t &= \lambda_p + \lambda_0, & \lambda_p + \lambda_0 &\leq \lambda_f; \\ \lambda_t &= \lambda_f, & \lambda_p + \lambda_0 &\geq \lambda_f. \end{aligned} \quad (5)$$

The straight lines in Fig. 2 clearly show that a single exponential decay was observed. The decay constant is $\lambda_t = \lambda_0 + \lambda_p$, and since λ_p is known, the observed values of λ_t determine the values of λ_0 .⁷

In Fig. 3 are shown the observed mean lives in the three oxidizing solutions as a function of concentration. The solid line is computed from Eq. (5) by assuming that λ_0 is proportional to concentration. The good fit of the experimental points to the solid curve is an indication that the process is correctly described by an oxidation rate which is proportional to concentration.

The flat part of the solid curve in Fig. 3 shows the limiting mean life $1/\lambda_f$, which should be the mean life of free positrons in these solutions. Since the densities of these solutions are all only slightly different from that of water, it is reasonable to assume that this mean life is close to the free positron mean life in water. Therefore the same value of $1/\lambda_f$ was used to draw all three curves; this value, 0.45×10^{-9} sec, was obtained from the average of the three shortest mean lives observed by Green and Bell in SbCl₃.

⁷ The density is small enough that the pickoff annihilation rate should be the same as in water, so $\lambda_p = 0.56 \times 10^9/\text{sec}$.

Since this limit could not be tested in the other solutions, the only check on this result is a value for the free positron mean life in water, obtained in 1953 by Bell and Graham.¹ Their value, 0.30×10^{-9} sec, is not in complete agreement with the present result; one would expect the mean life in water to be at least as great as, if not greater than, that in SbCl₃ solutions. But the disagreement is not too serious, for many uncertainties were necessarily involved in the measurement of this mean life by Bell and Graham. From the time distribution of the positron annihilations in water, they had to subtract the counts from the positrons annihilating with the long mean life, and then find the centroid of the remaining distribution, in order to compare its position with the position of the centroid of the "prompt" curve obtained from two simultaneous gamma rays. The "centroid shift" should be equal to the mean life. Thus in addition to uncertainties involved in subtracting the long-lived component, the measurement was subject to the serious systematic errors pos-

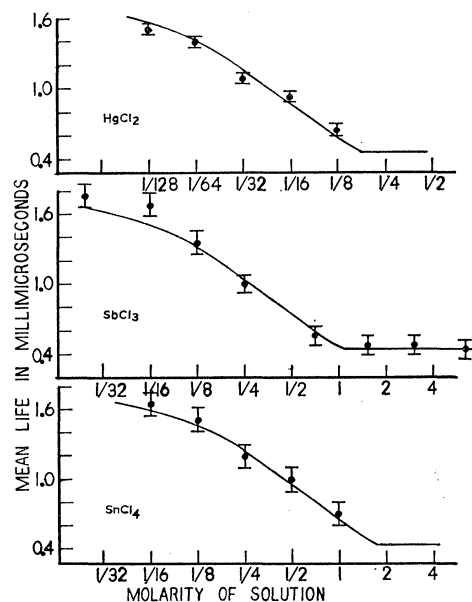
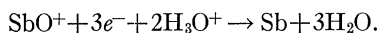


FIG. 3. Variation of positron mean lives with positive-ion concentration, compared to variation expected if oxidation rate is proportional to concentration (solid curve).

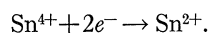
sible in the centroid shift method. A further check on these results would seem to be needed.

DISCUSSION

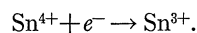
The correlation of mean life with oxidation potential is a strong indication that the process responsible for shortening the mean life is identical to the process of chemical oxidation. The chemical oxidation potential is, however, only a rough guide to the actual oxidizing power of the solution for Ps atoms. For example, the oxidation potential for SbCl_3 was obtained from the reaction



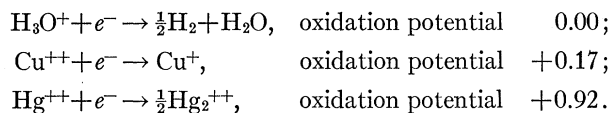
The Ps atom can supply only one of the three electrons needed for this process, and of course the density of Ps in the solution is so low that there is no chance of two or more Ps atoms taking part in any reaction. To take another example, the oxidation potential for SnCl_4 involves the reaction



But when Ps is oxidized by this ion, the reaction must be

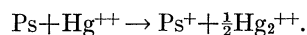


There is no way of determining the oxidation potential for this reaction chemically. However in many of the solutions used the oxidation potentials are known for reactions involving a single electron. The most significant of these are



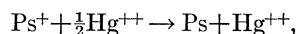
It is tempting to conclude that Ps may be assigned an "oxidation potential" whose value is between 0.00 and +0.17, because Ps is readily oxidized by the Cu^{++} ion and not by the H_3O^+ ion, according to the data on CuCl_2 and HCl solutions.

But such a conclusion would overlook the fact that a chemical reaction always proceeds in both directions. The quantity measured in this experiment was a reaction rate in only one direction—for example, the rate of the reaction



To determine that the oxidation potential of Ps is below -0.92, one would have to know that the speed

of the above reaction is greater than the speed of the inverse reaction,



under the same conditions of temperature, concentration of reactants, etc. But the inverse reaction is never observed in the case of Ps, because the product of the forward reaction, the bare positron, is removed from the solution by annihilation almost as soon as it is produced.

In the CuCl_2 solutions it was not even possible to obtain the reaction speed in the forward direction, because the oxidation effect is mixed up with the exchange effect in a mean-life measurement. Thus the only clue to the "oxidation potential" of Ps is the fact that the reaction rate in HCl solutions is too small to measure, while the rate must be at least 50 times as great in CuCl_2 solutions, as indicated by the fact that the oxidation was detected in the angular correlation measurement, which is less sensitive to this effect. The rate is not much greater than this even in HgCl_2 solutions, for which the oxidation potential is 0.75 v higher. Therefore the sharp difference in reaction rates between HCl and CuCl_2 solutions may mean that the oxidation potential of Ps lies between 0.00 and +0.17, but this is far from being established.

It would be a bit surprising if the oxidation potential, and thus the binding energy of Ps in solution, were greater than that of hydrogen, because the binding energy of free Ps is only one half that of hydrogen. This would mean that water reduces the binding energy of hydrogen much more than it reduces that of Ps. Further study of this possibility may give some insight into the nature of solutions.

Whether or not one is able to assign an oxidation potential to positronium, the use of positrons as a probe may give valuable information about the rates of ionic processes in solutions. This information seems to be unobtainable by other methods, which usually determine only relative reaction rates. Furthermore, because of the simplicity of the Ps atom, information concerning Ps reaction rates could be of special theoretical importance.

ACKNOWLEDGMENTS

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