THE TIME SPECTRA OF POSITRONS ANNIHILATING IN SOME ORGANIC LIQUIDS

by

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A thesis submitted in partial fulfilment of the requirements for the degree of Master of Science

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August, 1961

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Acknowledgments

I would like to express my sincere thanks to Dr. B. G. Hogg for his active participation in this experiment and for his many helpful suggestions.

Thanks are due also to Dr. G. E. Dunn for his part in discussions on the possible chemical nature of positron annihilation, and to Dr. E. H. Charlesworth for supplying many of the samples.

Finally, I would like to thank Alex Jakobschuk for constructing the limiters and the time to pulse height converter.

This work was supported by the Defence Research Board and the National Research Council.

Abstract

The intensity I_2 , and the mean life $\tilde{\ell}_2$ of the long lived component in positron decay have been measured in various organic halides using a fast time to pulse height converter. It was seen in most cases that the intensity of the long lived component was mainly dependent upon the halogen rather than upon the parent molecule. In general, compounds with a chlorine atom showed an I_2 of 14% - 16%, those with a bromine atom showed an I_2 of about 10% and those with an iodine atom showed an I_2 of about 4%.

The value of $\widetilde{\ell}_2$ for the chlorides studied varied from 1.10 nanoseconds to 2.04 nanoseconds. An attempt is made to correlate the $\widetilde{\ell}_2$ values with certain properties of the molecules.

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Chapter I INTRODUCTION

Since Deutsch (D-51) investigated the annihilation of positrons in gas@s, many groups have studied the process in liquids. The earliest results were obtained by DeBenedetti and Richings (De-52), and by Bell and Graham (B-53) in 1952 and 1953. Bell and Graham saw that liquids and some solids exhibited a complex decay scheme in which some of the positrons decayed with a mean life \mathcal{T}_1 of about 10^{-10} seconds, and the remainder with a mean life \mathcal{T}_2 of about 2×10^{-9} seconds. Deutsch (D-51) had earlier verified the existence of positronium (a positron-electron pair in a bound state) in gases; Bell and Graham explained their results by postulating the formation of positronium in these materials in spite of the fact that the orbital radius of a positronium atom is usually larger than the intermolecular spacings in condensed media.

According to this theory, positronium can be formed in the triplet state, (parallel spins) or in the singlet state (anti-parallel spins) for which the calculated lifetimes are of the order of 10^{-7} and 10^{-10} seconds respectively. From quantum mechanical considerations it has been shown that the decay from the triplet state must go exclusively via 3 quantum annihilation and decay from the singlet state must be by 2 quantum annihilation. Since Bell and Graham showed that their long lived component decayed by 2 quantum annihilation, they suggested that positronium which originally formed in the

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triplet state was being converted to the singlet state by collisions and was then decaying with the short lifetime of 10^{-10} seconds resulting in an effective lifetime of about 2×10^{-9} seconds. In their investigations they found originally that most materials with a \tilde{l}_2 component that were studied exhibited an I_2 (the percentage of positrons decaying with the longer lifetime) of about 30%. This was due mainly to a chance selection of materials and large errors. By 1957 the results of various workers (G-57) showed that I_2 varied from $\sim 2\%$ to 53%.

Green and Bell (G-57) performed experiments to measure variations in the intensity of the long lived component in water upon adding different concentrations of NO_3^- and $NO_2^$ ions. They saw that increasing concentrations depressed I_2 from its normal value in water of 21 \pm 5% to 2% without any appreciable change in $\tilde{\ell}_2$ and explained this by postulating the formation of positron compounds such as e^+ NO_3^- in the water. Positrons thus captured would decay with a lifetime similar to that of singlet positronium, i.e. 10^{-10} seconds, and hence would be lost from the $\tilde{\ell}_2$ component of the curve. The addition of other ions however, such as CI^- , left the I_2 relatively unchanged and the above chemical hypothesis did not hold true.

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In 1958, Hatcher, Millet and Brown (H-58) measured the mean life and the intensity of the long lived component in several organic compounds, both liquids and solids. They attempted to find a qualitative correspondence between the different values of I_2 and certain properties of the molecules and found a reasonably consistent correlation between I_2 and the force constant for the weakest bond in the molecules. They could also explain some of their results by postulating that a concentration of negative charge in the molecule would reduce I_2 by causing more positrons to annihilate with bound electrons.

equipment having a time resolution of about 2 nanoseconds, but recently types of apparatus have been developed having resolutions as small as a fraction of a nanosecond. This has enabled workers to see T_2 components where it was thought that none existed, and it would appear now that all materials exhibit a T_2 component.

Most of the above mentioned work was done with

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Chapter II <u>APPARATUS</u>

Sources:

A Na²² source, which emits a positron with a maximum energy of .541 Mev effectively in coincidence with a 1.28 Mev gamma ray, was used in the positron annihilation studies. The Na²² was in the form of an queous solution of Na²²Cl with a specific activity of 57 μ c/cc, obtained from Abott Laboratories in Chicago, Illinois.

Three different preparations of Na²²Cl were necessary in order to have positrons decay in water, aluminium and organic liquids.

For the decay of positrons in water, approximately $5 \ \mu c$ of Na²² were dissolved in a test tube of distilled water. No difficulty is encountered due to the fraction of positrons escaping from the water and annihilating in the pyrex glass since the decay schemes for positron annihilation in water and pyrex glass are very similar. (G-57).

To obtain some of the prompt coincidence curves, an aluminum sandwich source from A.E.C.L. was used. Other prompt coincidence curves were obtained with a Co^{60} source of about 5 µc.

With the exception of water, Na²²Cl was not solubly in any of the liquids studied, so an open source could be used. This consisted of a thin (3 mg/cm²)

roughened sheet of mica onto which 5 μ c of Na²² were evaporated over an area of about 1 cm². The mica sheet was then lowered into the solution to be studied.

With the apparatus used here, there would be no detectable long lived component for positrons decaying in mica. These would therefore add counts only to the prompt portion of the decay curve for the liquid being studied. Green and Bell (G-57) estimated that less than 10% of the positrons annihilate in the mica in a sandwich source of the thickness used in this experiment, so it is reasonable to assume that less than 5% annihilate in the mica in an open source.

General description:

The function of the apparatus is to measure the time delay between the emission of a 1.28 Mev gamma ray from the source and a .511 Mev gamma ray from the sample. This is a measure of the lifetime of the positron in the sample since a positron is emitted effectively in coincidence with the 1.28 Mev gamma ray, and the appearance of a .511 Mev gamma ray (or rather a pair of such gamma rays correlated at 180°) signifies the annihilation of the positron with an electron. Some 3 quantum annihilation does occur, but it is less than 1/2% of the total and can be ignored.

Fig. 1 shows a block diagram of the apparatus. In order that a count may be registered in the 100 channel -5-

FIG. I BLOCK DIAGRAM OF APPARATUS SAMPLE NE102 NE102 AMPLIFIER AMPLIFIER IP21 IP21 HAMNER N-301 SCINT. HAMNER N-301 SCINT. DISCRIMINATOR PULSE HEIGHT LIMITER LIMITER ANALY ZER TIME TO PULSE HEIGHT CONVERTER (|) (2)AMPLIFIER NE 5202 100 CHANNEL PULSE HEIGHT ANALYZER GATE PULSE GENERATOR SLOW COINC. SCALER H.V. NJE-S325 -6pulse height analyser, there must be a coincidence in the unit marked 'slow coincidence', and a pulse of sufficient amplitude to enter the kicksorter (after amplification) must come from the time to pulse height converter. The discriminator in the side channel marked 'l' is set to pass pulses to the slow coincidence unit proportional to energies greater than .52 Mev, and the pulse height analyser in side channel 2 is set to pass pulses proportional to energies between .2 and .5 Mev; i.e. side channel 1 accepts the compton distribution from 1:28 Mev gammas and side channel 2 accepts the Compton distribution from the .511 Mev annihilation radiation. If the two events occur within 0.5 microseconds of one another, then a gating pulse is sent to the kicksorter from the gate pulse generator. The number of such 'slow coincidences' is recorded on the scaler. Pulses from the 1P21 photomultipliers are sent to their respective limiters where they are changed to pulses of a constant height and length. These shaped pulses go to the time to amplitude converter, where, if they overlap, the amount of overlap is converted to a pulse height. This voltage pulse is then amplified and sent to the kicksorter where it is recorded if there has also been a slow coincidence. The bias is set on the kicksorter so that if the two pulses do not overlap, no count is registered even though a slow coincidence may have occured.

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Detectors:

The detectors consisted of plastic phosphors (NE 102) cemented with R 313 bonding agent to R.C.A. 1P21 photomultiplier tubes. The reason for employing a glue rather than silicon fluid will be discussed in Chapter 3. The plastic phosphors were cylindrical in shape, 2 cm. high by 2 cm. in diameter. A portion of the surface was ground to fit the face of the 1P21 photomultiplier. Although the counting efficiency and energy resolution is poor in these plastics, pulses of very short mean time duration ($\sim 2 \times 10^{-9}$ seconds) are produced. Plastic phosphors were chosen instead of stilbene crystals since they can be more easily machined. The plastics were wrapped with aluminum foil to provide diffuse reflection. The detectors were then made light tight by wrapping them with black scotch electrical tape.

The 1P21 photomultiplier tube is superior to conventional end window tubes since it has an internal photocathode and hence short transit time spreads. They also have the advantage of high gain. However, it would probably have been preferable to use a tube such as the R.C.A. 7264 which has a curved photocathode which results in almost spherical geometry. Good optical coupling to the

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scintillator is more easily obtained in these tubes than in those with internal photocathodes.

1P21 photomultipliers are normally operated at 900 volts but to ensure as small transit time variations as possible they were operated at 2300 volts. This was the maximum permissible voltage - anything higher resulted in the tubes going into continuous discharge. At this high voltage, noise pulses became excessive, so two of eight tubes available were chosen for best signal to noise ratio which was approximately 4 to 1 for 1.28 Mev gamma rays.

As shown in Fig. 2, a bleeder chain of 220 K resistors placed across a regulated high voltage supply determined the dynode voltages.

Limiters: (J-60)

The performance of the limiters is very critical in this type of fast coincidence circuit for reasons which shall be discussed in the next section. The limiter tube must be a sharp cut-off tube capable of producing a flat-topped anode pulse with a rise time of the order of 1 nanosecond. It must also be able to conduct a large d.c. plate current (15-20 milliamperes) in order that the fast rising pulse have an amplitude of at least 1 volt. A recently

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developed tube, the E 180 F, (a Philips tube marketed in North America under the number 6688) is suitable for this application since it has high gain, high current capacity, and a sharp cut-off. The limiter circuit as a whole must be such that the pulses produced are of a constant amplitude and independent of the counting rate.

Fig. 2 shows the circuit diagram for the limiters. The plate voltage is 175 volts which results in a plate current of 15 milliamperes. The screen is run at 70 volts and the screen current is about 4 milliamperes. Under these operating conditions the power dissipation of both the anode and the screen are kept within their rated maxima.

In d.c. operation the circuit has negative feed-back since the grid supply resistor is connected to the screen. If the screen current decreases, indicating reduced tube conduction and decreased plate current, then the screen voltage must rise. This results in an increase in grid current thus increasing the total tube conduction; i.e. connecting the grid supply resistor to the screen tends to stabilize the plate current helping to keep the amplitude of the output pulses constant.

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1. a.

Pulses from the photomultipliers are negative and of the order of 10 volts in amplitude. When such a pulse arrives at the grid of the E 180 F, the tube ceases to conduct and the voltage at the plate increases producing the required fast rising, flat-topped pulse about 2 microseconds long. The screen voltage also increases, charging the 68 mmf. decoupling condenser. However, the 1N56 diode is biased 2 volts positively (i.e. the screen voltage supply is adjusted by means of the 1 K potentiometer so as to be 2 volts more positive than the screen itself) so the positive excursion of the screen is limited. Therefore, when the screen reaches the screen supply voltage, the diode starts to conduct and clamps the screen to this voltage. When the tube again begins to conduct, the screen voltage drops to its normal value as the decoupling condenser discharges through the 27 K resistor with a time constant of $RC = 68 \times 10^{-12} \times 27 \times 10^3 = 1.8 \times 10^{-6}$ seconds. By having a small decoupling condenser, the screen voltage is able to recover in a short time . This aids in reducing counting rate effects.

Another factor minimizing these effects is the use of a negative high voltage supply on the photomultipliers. This eliminates the necessity of using a

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coupling condenser between the anode of the photomultiplier and the grid of the limiter tube.

The value of the grid supply resistor (220 K) is chosen so that the grid circuit is recharged to its normal d.c. voltage (0.5 volts) within approximately 1 microsecond after the end of the photomultiplier pulse. Since the grid is clamped, a fairly constant value of recharge current is supplied to the capacity between the grid circuit and ground after the grid has been charged negatively by the pulse from the photomultiplier. This results in very rapid decay of pulses applied to the grid. For example, a pulse that normally decays exponentially in about 20 microseconds decays at the grid in less than one microsecond. This is therefore another factor which minimizes counting rate effects.

The 2 microsecond long anode pulse travels to the junction of the shorting stub and the cable leading to the time to pulse height converter. Both are RG-7/U 97 ohm co-axial cables. The shorting stub is 400 cm. long; the speed of pulse transmission in this cable is 0.84 c, so a time of 32 nanoseconds is required for the pulse to reach the end of the stub, be reflected negatively and return to the junction. Thus, the resultant pulse to the

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converter is one whose length is 32 nanoseconds. Due to the output capacity of the limiter tube (10 mmf.) and stray capacities at the junction, there is a capacitive mismatch resulting in multiple reflections at the junction. By experimenting, it was possible to choose a terminating resistance in the time to pulse height converter that reduced reflections so they did not affect the operation of the converter.

Time to Pulse Height Converter:

The time to pulse height converter is a unit which converts the degree of overlap of two pulses into a voltage pulse; i.e. it converts the time interval between two pulses into a pulse height which can be recorded on a multichannel analyser.

The circuit used here (Fig. 3) is based upon one described by Bell(B-58) but it has several modifications. It employs a 6 BN 6 gated beam tube which has two control grids, g_1 and g_3 , called the signal or limiter grid and the quadrature grid respectively. The pulses from the limiter in the 1.28 Mev side channel are applied to the signal grid and those from the limiter in the .511 Mev side channel are applied to the quadrature grid.

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The electrode voltages on the 6 BN 6 are as follows: anode voltage, $E_a = 20$ volts; signal grid voltage, $E_{g_1} = 0.2$ volts; accelerator grid voltage, $E_{g_2} = 10$ volts; quadrature grid voltage, $E_{g_3} = 0$ volts and cathode voltage, $E_K = 1.0$ volts. Therefore, relative to the cathode, the signal grid has a negative bias of 0.8 volts, and the quadrature grid has a negative bias of 1.0 volt. In this application the tube is normally nonconducting. When the grids are driven positive from cut-off. the anode current increases towards a limiting value which is almost independent of further positive excursions of the grids. The grid voltage swing required for the plate current to reach its limiting value depends largely on the electrode voltages. With the low electrode voltages used, a 1.5 volt pulse on both grids is sufficient. However, the maximum pulse amplitude obtainable from the limiters is 1 volt which results in the 6 BN 6 operating in the knee of the ${\rm E}_{\ensuremath{\underline{\rm g}}\,1}\,vs.$ plate current curves when the tube is conducting. In this situation the value of the plate current is still affected by fluctuations in the amplitude of the limited pulses. One method of obtaining a sufficiently large limited pulse would be to use 185 ohm co-axial cable in place of the 97 ohm cable. This would give about a 2

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volt pulse but the rise time would be adversely affected, and reflections due to the capacitive mismatch at the junction on the limiter boxes would be increased. If the bias on the control grids was made less negative, then a l volt pulse would be large enough to drive the plate current to its limiting value, but then the increase in the plate current (and the decrease in the plate voltage) under pulsed conditions would be too small to be detected and integrated.

The operation of the complete converter circuit is as follows. An appreciable anode current will flow only if both grids are driven positive. Therefore, the tube conducts only when the limited pulses to the control grids overlap, the time during which conduction occurs being determined by the amount of overlap. While the tube is conducting, the voltage at the grid of the 5842 triode decreases with a time constant given by RC $\approx 10^4$ x 20 x 10^{-12} = 0.2×10^{-6} seconds. Since the overlap times measured are about 20 nanoseconds at most, the portion of the exponential decay curve being used is linear to a first approximation. Thus, the amplitude of the pulse at the grid and at the cathode of the 5842 is directly proportional to the length of the anode pulse at the 6 BN 6 which in turn is proportional to the amount of overlap of the limited pulses.

A considerable number of photomultiplier pulses are too small to be properly limited and these give rise to low voltage pulses at the output of the converter which are recorded on the small time delay side of the time spectrum (i.e. to the left of the centroid, eg. Fig. 7). For this reason, it is desirable to have the .511 Mev limited pulses arrive at the converter before the 1.28 Mev limited pulses so that longer delays will result in larger output voltages. These will then be recorded to the right of the centroid of the time spectrum. In fact, the 1.28 Mev gamma ray is emitted before the .511 Mev gamma ray so a delay of about 22 nanoseconds is inserted between the 1.28 Mev side channel limiter and the converter. There is also an invisible delay in the 6 BN 6 since the transit time of electrons from the signal grid to the quadrature grid is 5 nanoseconds at the operting voltages used. Therefore, the pulses from the 1.28 Mev detector are delayed by a total of 27 nanoseconds and the desired result is achieved.

Slow Coincidence Unit:

The slow coincidence unit also employs a 6 BN 6 gated beam tube. In this application the tube is operated at about the normal electrode voltages suggested

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in the General Electric Tube Manual. After being pulse height analysed, the pulses from the .511 Mev side channel are applied to the signal grid, and the discriminated pulses from the 1.28 Mev side channel are applied to the quadrature grid. In its quiescent state, the 6 BN 6 is non-conducting due to a negative bias on both control grids. When positive 5 volt pulses are applied to the control grids within .75 microseconds of one another, the tube starts conducting and a negative pulse is produced at the plate. After inversion, this pulse is applied to the grid of the first tube in a standard trigger circuit which finally produces a 15 volt, 3 microsecond long gating pulse. The output to the kicksorter is taken from a White cathode follower.

The number of chance slow coincidences is proportional to the resolving time of the coincidence unit. It is therefore desirable to make this time as small as possible. However, since there are relatively large variations in transit times through the amplifiers and pulse height analysers for pulses of different amplitudes, the true coincidence counting rate is seriously reduced if one attempts to use too small a time resolution.

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Circuit Performance:

A time to pulse height conversion curve is shown in Fig. 4. This curve was obtained by using Co^{60} 1.2 and 1.3 Mev gammas as a source of prompt coincidences. The positions of the centroids of the prompt coincidence curves were then plotted vs. the time delay inserted between the .511 Mev side channel limiter and the converter. The time to pulse height conversion is linear over a range of about 16 nanoseconds. However, there appeared to be a slight sinusoidal shape to some of the calibration curves which could be due to a ringing of the limiter pulses (J-60). As was mentioned earlier, the time to pulse height converter is amplitude dependent. Therefore, if high frequency transient rings were superimposed on the limited pulses, the converter output voltage would be dependent on the relative phases of the transient rings as well as the amount of overlap of the limited pulses. This fault never became serious enough to affect the experimental results and hence no attempt was made to correct it.

Fig. 5 shows 2 time resolutions curves, one obtained by pulsing the grids of the limiters simultaneously with a 60 cycle pulse generator, and the other obtained using Co^{60} as a source of prompt coincidences. The electronic

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resolution (full width at half maximum) is 0.1 nanoseconds, and the resolution using a Co^{60} source is 1.3 nanoseconds. The right hand side of the Co^{60} resolution

curve falls from any value of the counting rate to one half that value in 0.2 nanoseconds. It is this slope as well as the resolution that ultimately limits the value of \mathcal{T}_2 and I_2 that can be measured with reasonable accuracy. For good results, the \mathcal{T}_2 of the substance under investigation should be about 10 times the natural slope of the resolution curve.

The long term stability of the apparatus was very good if the room temperature was kept within a range of about 10° C. Time calibrations were made every 2 to 4 days and over a period of 3 weeks there was no appreciable change in the time sensitivity of the equipment. The side channels were also calibrated periodically (about once a week) using the .662 Mev gamma ray from Cs¹³⁷. It was assumed that the energy response of the detectors was linear, so, knowing the voltage corresponding to an energy of .662 Mev, the voltages corresponding to .2 and .5 Mev were obtained by extrapolation. These points were also quite stable over a 3 week period.

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Experimental Procedure and Data Processing:

For most of the runs, two samples were used, each containing a 5 μ c Na²² source. Two individual sources were used since one source with the same total amount of activity would have been too thick. This would have given rise to 2 problems: a considerable percentage of the positrons would annihilate in the Na²²Cl instead of in the sample, and the Na²²Cl would be more likely to flake off the mica sheet. One sample was mounted on either side of the detectors.

Runs were usually 8 to 10 hours long during which time approximately 80,000 counts were accumulated. In such a run, the background due to chance slow coincidences was 30 to 40 counts per channel where 1 channel corresponded to 0.3 nanoseconds. Since the time to pulse height conversion was linear over at least twice the range necessary to record the time spectrum, the background was easily determined.

The method of curve analysis followed that of Green and Bell (G-57). After the background had been subtracted, the curve (coincidence counts vs. delay) was plotted on semi-logarithmic paper as in Fig. 7. A straight line was then drawn through the points on the tail (the χ_2

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portion of the curve). Usually there was no difficulty in positioning the straight line by eye, but at times it was necessary to use a least squares fit. For the former case the mean life of the long lived component is given by

$$\widetilde{l} 2 = \frac{.434}{\text{slope}}$$

and in the latter case $\mathcal{L}_2 = \cdot 434 \frac{\left[\mathcal{E}_{x_i}^2 - \frac{1}{n} (\mathcal{E}_{x_i})^2\right]}{\frac{1}{n} \mathcal{E}_{x_i}^x \mathcal{E}_{y_i} - \mathcal{E}_{x_i}^x \mathcal{Y}_i}$

where

 x_i = time delay of the i th point.

n = number of points used in the analysis.

The position of zero time delay was determined from the centroid of an aluminum curve corrected for the lifetime of positrons in aluminum. The tail was then projected back to this point. I_2 , the intensity of the long lived component, is the ratio of the area under the tail (including the area under the projected line) to the area under the total curve, both of which were obtained by numerical integration.

Chapter III

FACTORS EFFECTING THE TIME RESOLUTION

The resolving time of the apparatus may be limited by the detectors, or by the associated electronics.

Considering first the detectors, Fig. 6 illustrates the effect of the quality of optical coupling between the phosphor and the photomultiplier tube on resolution. Curve 'a' was obtained using silicon fluid for optical coupling. In this case no effort was made to ensure that the optical joint was free of air bubbles, or even that the silicon fluid covered the entire face of the phosphor. Curve 'b' was obtained after the phosphors were carefully cemented to the photomultiplier tubes. Whether or not good optical coupling has been achieved is easily seen by looking through the back of the scintillator at the photocathode.

Post and Schiff (P-50) have shown that the mean time delay for the appearance of the first photoelectron from the photocathode is given by

 $\overline{t} = \frac{\gamma}{R} (1 + \frac{1}{R})$ (for R >> 1)

where $\widetilde{\mathcal{L}}$ is the mean life of the scintillation in the phosphor, and R is the number of photoelectrons produced.

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The number of photoelectrons produced is proportional to the number of photons striking the photocathode which in turn is proportional to the energy expended in the phosphor assuming perfect optical coupling. However, if the optical coupling is not good, the number of photons reaching the photocathode (for the same amount of expended energy) and the resulting number of photoelectrons will be decreased, thus increasing \tilde{t} . With a larger \tilde{t} , the uncertainty in the time of emission of the first photoelectron increases and this adversely affects the resolution. One would therefore expect a broadening of the resolution curve as is seen in Fig. 6. The appearance of the tail on the right hand side of the curve is not explained by the above considerations and further experiments are being planned to investigate this effect.

It was stated earlier that, in the .511 Mev side channel, only pulses proportional to energies between .2 and .5 Mev are allowed to pass to the slow coincidence unit. The reason for this can be seen from the above equation. If energies lower than .2 Mev are accepted then R again becomes small, \bar{t} becomes large and the resolution curve is broadened.

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It is also clear from the equation why a phosphor such as NE 102 or stilbene with a small γ must be used.

Another factor affecting the resolution is the variation in transit time of electrons in the photomultiplier tube. In order to minimize this effect the photomultipliers were operated at 2300 volts with a high stability supply.

Chapter IV

EXPERIMENTAL RESULTS AND DISCUSSION

Time spectra of positrons annihilating in hexane and its halogen derivates were taken, and the data was analysed for \tilde{L}_2 and I_2 after the fashion described in Chapter II.

The experimental curves for the hexane family are shown in Fig. 7. Measurements on the propyl halides and the phenyl halides, which had been done previously by Ormrod, (0-60) and by Millet (H-58) respectively, were repeated and the results of these measurements are shown in table I.

The results obtained in this work on the phenyl halides agree within experimental error with those of Millet, while the results on the propyl halides obtained here are different from those of Ormrod. Ormrod's results were obtained under experimental conditions where the optical coupling was of dubious quality, and hence could lead to values of I_2 that were too large. His results clearly indicate this trend when compared with the new data.

From this table it is seen that the chlorides

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TABLE I

Decay of Positrons in the Hexyl, Phenyl, and Propyl Halides

Sample	I ₂ (
	This Work	Others	
Hexane	38 ± 2		
l-Chlorohexane	16 ± 2		
l-Bromohexane	10 ± 2		
l-Iodohexane	4 ± 2		
Benzene	34 ± 2	35 ± 2	
Chlorobenzene	15 ± 2	14 ± 2	; (H-58)
Bromobenzene	9 <u>+</u> 2	6 <u>+</u> 2)	
l-Chloropropane	16 ± 2	23 ± 4)
1-Bromopropane	10 ± 2	16 ± 4	((0-60)
2-Iodopropane	4 ± 2	12 ± 4	J

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exhibit an I_2 of about 16%, the bromides an I_2 of about 10%, and the iodides an I_2 of about 4%. The appearance of this regularity led to the investigation of the other chlorides included in table II. All of these exhibited an I_2 of 14% to 16%. The parent molecules in these compounds have widely varying structures, and the percent volume occupied by the chlorine atom also varies. It appears therefore, that the value of I_2 is dependent almost completely upon the halogen atom rather than upon any property of the molecule as a whole.

This is not true however, for the values of \mathcal{T}_2 . An investigation was carried out into the variation of \mathcal{T}_2 in a number of organic chlorides. The results are shown in Fig. 8. \mathcal{T}_2 ranges from 2.04 nanoseconds in tert. butyl chloride to 1.10 nanoseconds in α -chlorotoluene.

Millet (H-58) was unable to observe a long lived component in α -chlorotoluene probably because of poorer time resolution. Even with the present apparatus, the results in the case of compounds where the \mathcal{T}_2 is less than 1.5 nanoseconds are not as reliable as in cases where \mathcal{T}_2 is larger. As was mentioned in Chapter II, this is due to the fact that, as \mathcal{T}_2 becomes small, the slope of the tail approaches the natural slope of the resolution curve.

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It then becomes difficult to determine the point at which the tail begins, and hence results could be in error.

It was thought that the reduction of \mathcal{C}_2 could be due to either a change in the binding of the halogen to the parent molecule, or a change in structure of the molecule.

In the former case, one thinks of the positron rupturing the carbon-halogen bond, forming a compound such as e^+Cl^- and then annihilating. Another process could be one in which the positron becomes bound to the chlorine atom, ruptures the bond at a later time and then annihilates. If such were the case, it would not be unreasonable to expect some dependence of \mathcal{T}_2 on the carbon-chlorine bond strength.

The first five compounds (with the larger \mathcal{T}_2 's)shown on Fig. 8 have bond dissociation energy values for the carbon-chlorine bond of about 75 kilocalories per mole, and the last (with the smallest \mathcal{T}_2) has a value of about 68kcal./mole. However, chlorobenzene, with an intermediate \mathcal{T}_2 has the largest bond dissociation energy (86 kcal./mole). This indicates that no dependence of \mathcal{T}_2 on bond strength exists and that no positron compounds are formed in these cases. If such positron compounds were

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formed, one would also expect the value of I_2 to be affected by the carbon-chlorine bond strength, but, within, experimental error, no such change was observed.

Fig. 9 shows the structure of some of the organic chlorides studied. In tert. butyl chloride, the chlorine atom is buried relatively deeply in the molecule having a hydrogen atom on either side of it. The structure of chlorocyclohexane is such that the chlorine atom is still well protected but to a slightly lesser extent. Chloropropane, chlorohexane and amyl chloride are all aliphatic compounds with the chlorine atom situated much the same in each case but protruding slightly more than in chlorocyclohexane. In chlorobenzene, which has a ring structure, the chlorine atom protrudes even more but remains in the plane of the In α -chlorotoluene, hydrogen atoms are again fairly ring. close to the chlorine atom, but the $\mathrm{CH}_2\mathrm{Cl}$ group can rotate such that the chlorine atom is projecting out of the plane of the benzene ring; i.e. the chlorine atom may become quite exposed.

Thus, there appears to be fairly good correlation between the values of \mathcal{T}_2 and the extent to which the chlorine atom protrudes from the molecule.

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Table II shows the results for all the compounds studied.

No long lived component was observed in bromoform. This result was expected since the presence of even one bromine atom in a molecule reduces I_2 considerably. One would therefore expect that 3 bromine atoms would quench out almost all the $\tilde{\chi}_2$ component.

Two sulphur compounds were studied n-hexyl sulphide and n-propydisulphide. It is interesting to note that the compound with one sulphur atom (n-hexyl sulphide) which has an even number of electrons and one less electron than chlorine, exhibits a larger I_2 than does a compound with one chlorine atom. Again it is not surprising that n-propyldisulphide has a small I_2 since there are 2 sulphur atoms per molecule.

Preliminary investigations into the effects of F centres produced in NaCl single crystals on positron decay yielded no results because of inadequate time resolution. A betterment of resolution by a factor of 2 would make the experiment possible.

Concluding Remarks

The factor chiefly responsible for the

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Su	ummary of Results	
Samp le Water Hexane	$I_2(\%)$ 24 ± 2 38 ± 2	$\gamma_{2}(10^{-9} \text{ sec})$ 1.80 ± .05 2.25 ± .05
1-Chlorohexane	16 ± 2	1.93 ± .05
l-Bromohexane	10 ± 2	1.9 ±.1
l-Iodohexane	4 ± 2	1.8 ± .2
n-Hexyl sulphide	26 ± 2	2:4 = .1
n-Propyldisulphide	8 ± 2	2.1 ±.1
Chlorocyclohexane	15 ± 2	1.98 ± .05
l-Chloropropane	16 ± 2	1.97 ± .05
l-Bromopropane	10 ± 2	1.8 ± .1
2-Iodopropane	4 ± 2	1.8 ±.2
Propylene oxide	19 ± 2	2.2 ± .1
Benzene	34 ± 2	2.20 ± .05
Chlorobenzene	15 ± 2	1.50 ± .05
Bromobenzene	9 ± 2	1.6 ± .1
Bromoform	unobser	ved
n-Amyl chloride	15 ± 2	1.82 ± .05
tert. Butyl chloride	16 ± 2	2.04 ± .05
α -Chlorotoluene	14 ± 2	1.10 ± .05
Errors quoted are not	absolute but are for	comparison
purposes.		

TABLE II

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variation in I_2 in organic halides is the halogen atom. The factor chiefly responsible for the variation in \mathcal{C}_2 appears to be the structure of the molecule.

It would be interesting to investigate the decay of positrons in 3 other organic chlorides, namely allyl chloride, vinyl chloride and chloroacetylene. The bond dissociation energy for the carbon-chlorine bond in allyl chloride is relatively small (58 kcal./mole) and in vinyl chloride it is quite large (104 kcal./mole). A test of these compounds would probably indicate more clearly whether or not the bond strength affects the mean life of the positron.

Chloroacetylene has an unusual chain structure in that the chlorine atom is at the end of the chain with no hydrogen atoms in the vicinity. A test of this compound could therefore supply more conclusive evidence as to what effect the structure of the molecule has on \mathcal{T}_2 . This compound, however, boils at -30°C and the present apparatus would have to be modified for this type of investigation.

The time resolution of circuits is improving and it is being shown that \mathcal{C}_2 components exist where before they were unobserved. The stability of the electronics involved is now sufficient that runs of the order of several

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days can be made. Thus, precise measurements are now possible even in unusual environments, such as cryostats and furnaces, where extremely low counting rates due to geometry are met.



References

- B-53 Bell, R. E. and Graham, R. L., Phys. Rev. <u>90</u> 644 (1953).
- B-58 Bell, R. E. and Green, R. E., Nuclear Instrum. <u>3</u> 127 (1958).
- D-51 Deutsch, M., Phys. Rev. 82 455 (1951).
- De-52 DeBenedetti and Richings, Phys. Rev. 85 377 (1952).
- G-57 Green and Bell, Can. J. Phys. <u>35</u> 398 (1957).
- H-58 Hatcher, Millet and Brown, Phys. Rev. 112 1921 (1958).
- J-60 Jones, G., Ph.D. Thesis, University of British Columbia, 1960.
- 0-60 Ormrod, J. H., M.Sc. Thesis, University of Manitoba, 1960. J. Chem. Phys. <u>34</u> 624 (1961).
- P-50 Post and Schiff, Phys. Rev. 801113 (1950).

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