THE REACTION OF ORTHO-POSITRONIUM
WITH NITROAROMATICS
VIA COMPLEX FORMATION

by

William Juul Madia

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APPROVED:

Hans J. Ache, Chairman

John G. Mason

Michael A. Ogliaruso

John C. Schug

Jimmy W. Viers

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Blacksburg, Virginia

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INTRODUCTION

The chemical consequences of a nuclear transformation such as electronic excitation, ionization, and bond cleavage allow one to study the effect that such an event has on a particular system. This area is generally referred to as nuclear or radiation chemistry. However, there are certain nuclear transformations that are directly influenced by the physical and chemical nature of their environment. The two most notable of these are the Mössbauer effect and positron annihilation. The study of these types of phenomena cannot be classified as the chemical effect <u>of</u> a nuclear transformation, but rather as the chemical effect <u>on</u> it. The physical and chemical properties of a system alter the rate of positron annihilation and allow the positron to be used as a probe of its environment. For example, recent work in this area has used the positron to measure the electron momentum distributions in certain aliphatic liquids. It is also applicable to the solid state where positron lifetimes have been useful in estimating the concentration of lattice defects in semi-conductors.

The positron itself is a stable particle, but life in one's antimatter world is quite short, typically a fraction of a nanosecond in the condensed phase. By forming a bound state with an electron whose spin is triplet relative to the positrons' (ortho-positronium), the positron may experience a tenfold enhancement in its lifetime.

A rapid reaction in solution has previously been observed between ortho-positronium and certain diamagnetic organic molecules such as nitroaromatics and quinones. They react rapidly with second-order rate constants typically three orders of magnitude greater than most diamagnetic compounds.

The focus of this research is to determine the mechanism by which ortho-positronium reacts with a certain class of compounds, the nitroaromatics, and to evaluate any of the pertinent conditions necessary for this process.

Determining the nature of this process becomes possible by studying the variation in the positron lifetime distribution on dissolution of small amounts of these compounds in suitable solvents. The role that substituents play will be examined from both a steric and reactivity viewpoint. Investigating the temperature dependence of these reactions will also be helpful. Quantum mechanical calculations will be performed to study the stability of positron and positronium complexes with diamagnetic organic molecules.

REVIEW OF BASIC PRINCIPLES

A. The Positron

One of the most interesting consequences of the theory of relativity is the division of the universe into matter and anti-matter. Dirac[1] has shown by purely theoretical arguments that the relativistic wave equation for a free electron has both positive and negative energy solutions. The magnitude of these solutions is at least $m_e c^2$, where m_e is the mass of the electron and c is the speed of light. Instead of disregarding the negative solution, he proposed that it corresponded to a particle with a mass equal to that of an electron but carrying the opposite charge -- a positron. Two years later, Anderson[2] discovered the positron in cloud chamber tracks of cosmic radiation.

The positron states can be intuitively understood in terms of the "theory of holes." Since electrons are observed only in positive energy states, the theory requires that the negative energy states be completely filled with electrons. A photon with energy greater than $2\ m_e c^2$ could raise an electron from its negative energy state to a positive one. The "hole" created by this transition in the "sea" of electrons would behave as a positron in that it is defined to have negative energy, negative momentum, and spin opposite to the electron.

There is a second interpretation of the negative energy solution which is equally valid and does not require an unobservable "sea" of electrons. The positron, instead of being a negative energy "hole," can be described as an electron moving backwards in time.[3] At the present level of our understanding, the latter interpretation has no physical meaning.

B. Positron Decay

The emission of a positron from a radioactive nucleus is referred to as positron decay. It occurs in nuclei that are proton rich in relation to their most stable isobars. The creation of a positron arises from the transformation of a proton, p, within the nucleus into a neutron, n, a positron, β^+, and a neutrino, ν, with an accompaning decrease in the atomic number of the parent nucleus by one unit.

$$p \rightarrow n + \beta^+ + \nu \qquad (1)$$

The positron cannot exist within a nucleus, because of difficulties arising from the considerations of angular momentum conservation, and is emitted. Once the positron has left the nucleus, it is repelled by the Coulombic interaction between itself and the positively charged nucleus. The release of binding energy during positron decay along with the Coulomb effect cause the positron to possess a considerable amount of kinetic energy. This may range from a few hundred keV up to several MeV.

The parent and daughter nuclei are in definite energy states for positron decay. Energetically, in order for positron decay to take place, the atomic mass of the parent nucleus, M_p, must be greater than the sum of the rest masses of two beta particles and the atomic mass of the daughter nuclei, M_d.

$$M_p > M_d + 2m_e \tag{2}$$

A neutrino is emitted simultaneously with the positron. Therefore, the energy spectrum of emitted positrons is continuous rather than having a discrete value. The positron energy spectrum[4] for sodium-22 is shown in Figure 1. The maximum energy, also referred to as the end-point energy, is 0.544 MeV. In general, the maximum number of positrons emitted in the energy distribution occurs at one-third of the end-point energy. The remaining energy is divided between the recoil energy of the daughter nucleus and the neutrino energy.

The elementary theory of beta decay, according to the basic transformations involved, was first given by Fermi.[5] His descriptive ideas gave satisfactory explanations for the shapes of beta particle energy spectrums, half-lives,

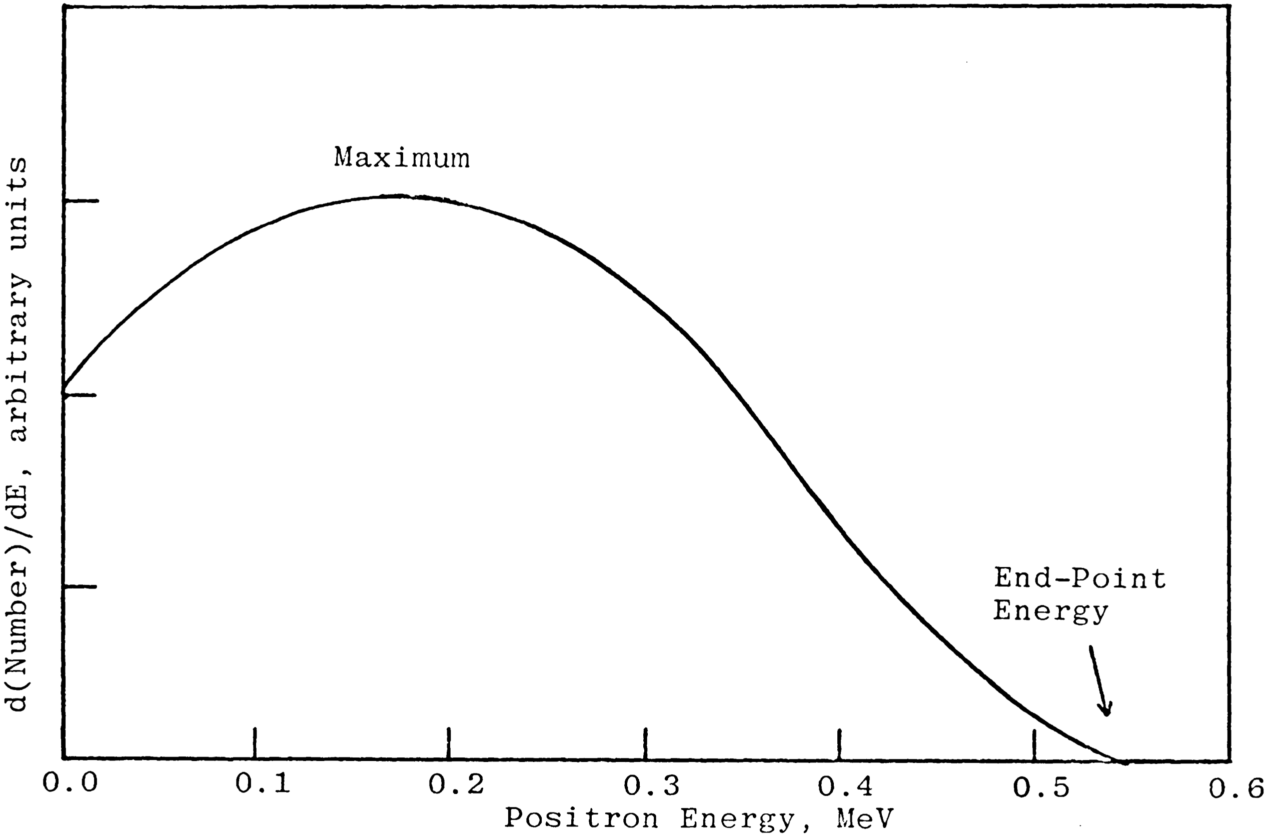


Figure 1. Energy Spectrum of Positrons Emitted from Sodium-22. (from Ref. 4)

etc. A more modern theory, which takes into account the nonconservation of parity, has been developed by using relativistic quantum mechanics and was introduced by Lee and Yang.[6]

Positrons, like all charged particles, lose their energy while passing through matter. Their interactions can induce ionizations and excitations in the stopping medium. Energy losses due to bremsstrahlung dominate only at higher energies.[7] Tao and Green have estimated that a high energy positron interacting with a dense material such as water will be slowed down to the first ionization energy of water in 7 psec. The total time needed to thermalize the positron was roughly estimated to be 100 psec. The interactions of positrons with matter are difficult to study at very low energies because of the competing process of mass annihilation whose cross-section is greatest for thermalized positrons.

C. Positron Annihilation

Annihilation is an event unique to matter-anti-matter pairs such as the electron-positron. However, it has been shown by Goldanskii[8] that fewer than five percent of the positrons emitted into a condensed medium will annihilate during the slowing down process. According to the theory of positron annihilation,[9] one, two, or three photons may be emitted as the result of a collision between a positron and an electron. If the two particles meet with their spins antiparallel, two photon emission results. Two photon emission is forbidden for collisions where the two particles meet with their spin parallel and three photons are emitted. Emission of a single photon requires that a third body, M, be present to absorb the recoil momentum of the annihilation photon.

$$e^{+} + e^{-} + M \rightarrow \gamma + M \tag{3}$$

In order to be complete, it should be noted that if two such bodies, M, are present, annihilation may occur without the creation of electromagnetic energy.

$$e^{+} + e^{-} + 2M \rightarrow 2M \tag{3a}$$

The probability of such an occurance is very small and it has never been observed.

Goldanskii has characterized the three basic mechanisms by which slow-positrons are annihilated.[8]

First, annihilation as "free" positrons in collisions with electrons of their surroundings.

The cross section for the two photon annihilation of a positron and an electron, $\sigma_{2\gamma}$, was first calculated by Dirac.[1] He assumed in the calculation, that the electron of the annihilating pair was at rest. The velocity, v, of thermal positrons is small (6.6×10^{6} cm/sec) compared to the speed of light and the equation reduces to

$$\sigma_{2\gamma} = \sigma_s = \pi r_o^2 \, c/v \tag{4}$$

or

$$\sigma_{2\gamma} v = \pi r_o^2 c = \text{constant} \tag{4a}$$

where $r_o = 2.8 \times 10^{-13}$ cm is the classical radius of a beta particle.

The two gamma annihilation rate in a multi-electron system is

$$\lambda_{2\gamma} = \lambda_s = \sigma_{2\gamma} v \rho N_o Z_{EFF}/M \tag{5}$$

where ρ is the density, N_o is Avargadro's number, M is the molecular weight, and Z_{EFF} is the effective number of electrons seen by the positron (usually this is taken to be the number of valence electrons). The annihilation rate in water, assuming $Z_{EFF} = 8$, is calculated at 2.2 nsec^{-1} and corresponds to a free positron lifetime of 0.46 nsec. This value agrees very well with experimental results.[10] Annihilation rates in the gas phase are usually two to three orders of magnitude less, due to lower densities.

The triplet interaction usually results in three photon emission. Ore and Powell[11] in 1949 were the first to correctly calculate the ratio of two photon to three photon annihilation rates as 1115. The much lower triplet rate, λ_T, is caused by the multiple character of the three quantum process. The ratio of the cross sections for these two modes of decay is one-fourth the ratio of the annihilation rates (see p. 13). Summarizing,

$$\lambda_S/\lambda_T = 1115 \quad ; \quad \sigma_S/\sigma_T = 372 \qquad (6)$$

A second channel of annihilation involves the binding of a positron to a multi-electron system. This should cause polarization of the electron shells and subsequent formation of positron atomic or molecular orbitals. Much theoretical work in this area is being performed and Chapter 4 of this work deals with this subject.

D. Positronium

The most widely studied interaction of slow positrons with matter is the formation of positronium, Ps, a hydrogen-like bound state of a positron and an electron. This species was proposed by Mohorovicic in 1934[12] to account for the unusual emission spectra of some nebulae. The ionization potential of ortho-positronium was calculated to be 6.77 eV by Ruark,[13] and he also proposed the name positronium for the e^+e^- atom.

In order to treat positronium as the structural analogue of hydrogen, the reduced mass of hydrogen, $\mu_H \simeq m_e$, must be replaced by the reduced mass of the positronium atom, $\mu_{Ps} = m_e/2$. The Bohr radius, a_{Ps}, is 1.06 Å, twice that of hydrogen, and the first ionization potential, binding energy, is half as great in positronium as in hydrogen.

The two ground, n = 1, spin states of positronium are the singlet, para-positronium (p-Ps) and the triplet, ortho-positronium (o-Ps). Figure 2 illustrates both forms and lists some of their characteristics. The average lifetime of these two atoms in free space can be calculated from the rates of singlet and triplet annihilation given in Eq. (5) and (6). To do this, the factor, $\rho N_o Z_{EFF}/M$, must be replaced by the density of the electron wave function at the positron, $|\psi(o)|^2$. Eq. (5) now becomes

$$\lambda_s^o = 4\pi r_o^2 c|\psi(o)|^2 = 1/\tau_s^o \qquad (7)$$

In a free ground-state atom of positronium

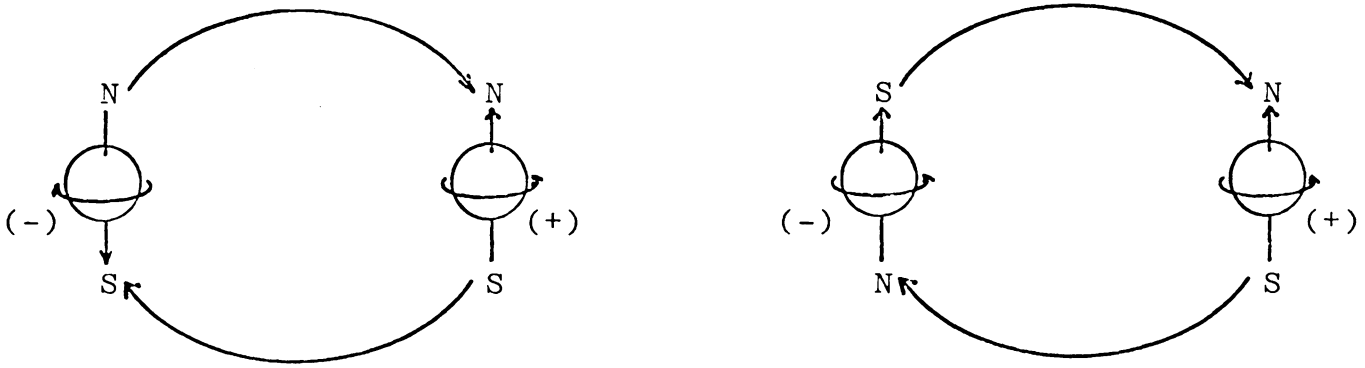
$$|\psi(o)|^2 = (1/\pi a_{Ps}^3) = (1/\pi)(\mu_{Ps}e^2/\hbar^2)^3 =$$

$$2.68 \times 10^{23}\ \mathrm{cm}^{-3}$$

and therefore

$$\tau_s^o = 0.125\ \mathrm{nsec} \qquad (8)$$

for a para-positronium atom in free space. Para-positronium has a shorter lifetime than that of free positrons in most



Para-Positronium

Singlet state ^1S
Spins are antiparallel
Magnetic poles are parallel
Disintegrates into 2 photons
Mean-life = 0.125 nsec

Ortho-Positronium

Triplet State ^3S
Spins are parallel
Magnetic poles are antiparallel
Disintegrates into 3 photons
Mean-life = 140 nsec

Figure 2. Some Physical Properties of Para- and Ortho-Positronium.

substances, the latter has $\tau_F \simeq 0.45$ nsec in condensed matter. An ortho-positronium atom in free space has a calculated mean lifetime[11]

$$\tau_T{}^{o} = 140 \text{ nsec} \tag{9}$$

This value is 1115 times longer than the mean lifetime of the singlet atom.

The four ground state wave functions of positronium, $\psi_{J,m}$, are composed of both positron and electron moieties. They are given in Eqs. (10). Para-positronium has a total momentum, $J_S = 0$, and a magnetic quantum number, $m = 0$. There are three substates of ortho-positronium, $J_T = 1$, with $m = +1, 0, -1$.

$$\begin{aligned}
\psi_{0,0} &= (1/\sqrt{2})\{\chi_-(1)\chi_+(2)-\chi_-(2)\chi_+(1)\} \quad {}^1S_o \\
\psi_{1,1} &= \chi_-(1)\chi_+(1) \\
\psi_{1,0} &= (1/\sqrt{2})\{\chi_-(1)\chi_+(2)+\chi_-(2)\chi_+(1)\} \quad {}^3S_1 \\
\psi_{1,-1} &= \chi_-(2)\chi_+(2)
\end{aligned} \tag{10}$$

Statistically, ortho-positronium should be formed in 75% of the atoms with para-positronium formation occuring 25% of the time. The factor, $|\psi(0)|^2$, in Eq. (7) can now be more correctly defined to be the density of electrons whose spin is antiparallel to that of the positron. In a multi-electron system, this factor would only be 1/4 of that for para-positronium, hence the need for the additional factor of 4 in Eq. (7).

The theory of the formation of positronium in the gas phase, as developed by Ore[14] places certain energy restrictions on this process. The narrow energy region where positronium formation is allowed is called the Ore gap. Formation of positronium can be represented as follows:

$$e^{+} + M \rightarrow Ps + M^{+} \qquad (11)$$

A positron collides with a molecule, M, removes an electron from it, and forms positronium. The probability of ionization as described in Eq. (11a) predominates over positronium formation if the positron has kinetic energy greater than the ionization energy of the molecule, I.

$$e^{+} + M \rightarrow e^{+} + e^{-} + M^{+} \qquad (11a)$$

This energy level is considered to be the top of the Ore gap, the upper kinetic energy limit at which positronium formation can occur. If the kinetic energy of the positron is greater than the first excitation potential, E*, of M, electronic excitation of the molecule could occur and would compete with positronium formation.

$$(e^{+})^{*} + M \rightarrow e^{+} + (M)^{*} \qquad (12)$$

If the ionization potential of M is greater than the binding energy of positronium, 6.8 eV, the reaction is endothermic. Only positrons possessing enough kinetic energy, $E_{Kin} > I - 6.8$, can form positronium. This makes, I-6.8, the lower positron energy threshold, T, for positronium formations.

The Ore theory is based on three basic assumptions:

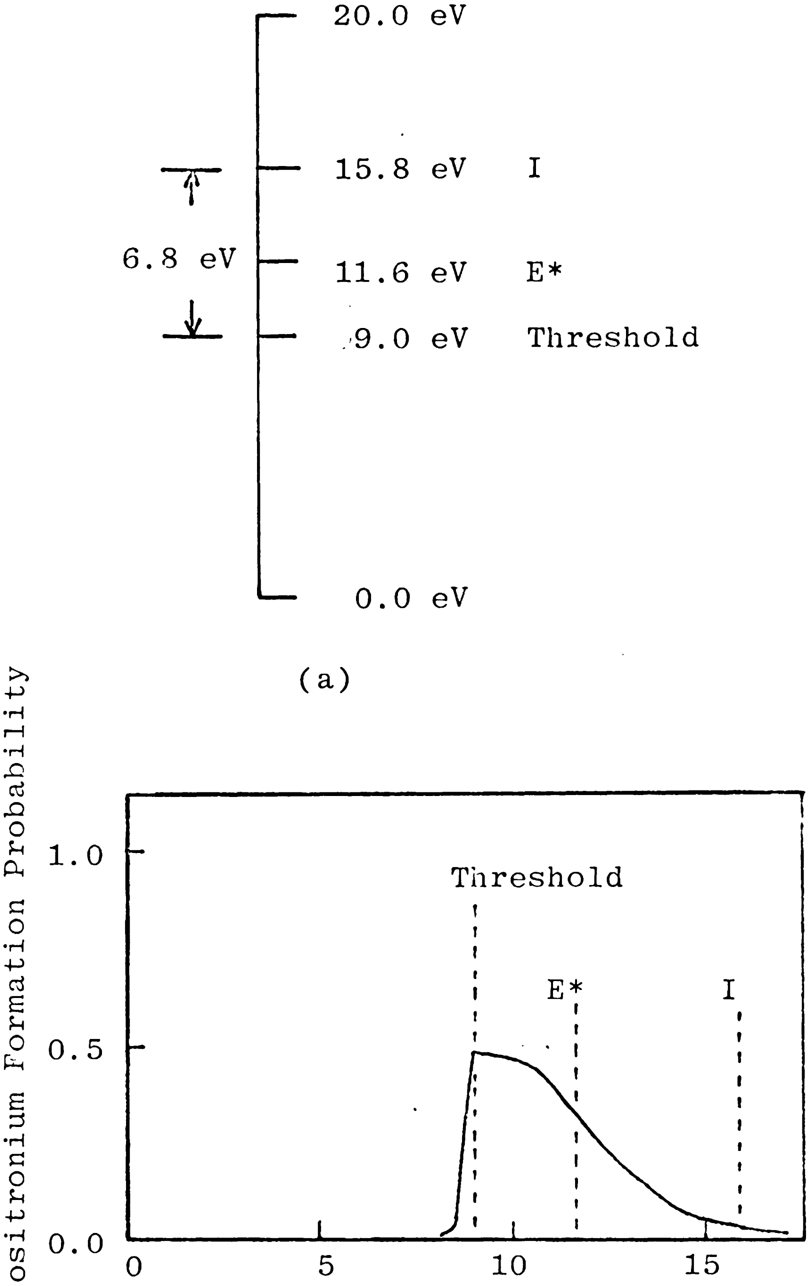
(1) All positrons reach the top of the Ore gap, I, without being annihilated.

(2) There is a statistical distribution of positron energies in the range between I and E = thermal.

(3) All positrons whose kinetic energy lies within the Ore gap will form positronium.

Figure 3a is an energy diagram showing the Ore gap in gaseous argon and Figure 3b is a plot of the hypothetical dependence of the positronium formation probability in argon gas as a function of positron energy.[15] Green and Lee note that the curve is meant to illustrate general features only. The actual formation probability has been measured by Gittleman[16] in a variety of gases and was found to average about 30% of positrons emitted.

Since the binding energy of positronium is less than the ionization potential of most molecules, a considerable number of positrons exist with energies below the Ore gap.



(a)

(b)

Figure 3. (a) Energy Diagram of the Ore Gap and (b) Hypothetical Positronium Formation Probability in Gaseous Argon. (from Ref. 15)

The Ore theory does not place any energy restriction on positron complex formation and positrons may bind to molecules at any energy. Positron complex formation above or within the Ore gap causes inhibition of positronium formation. However, positron complexes are generally thought to form in the energy region beneath the Ore gap due to the lower positron energy and lack of competition with positronium formation.

E. Quenching

Quenching is any means by which the positronium lifetime is shortened from its self-annihilation lifetime as described in the previous section. Quenching occurs in all systems and is most noticeable for the long-lived ortho-positronium. The ortho-positronium lifetime in free space, 140 nsec, may be shortened to a few tenths of a nanosecond in condensed phases. There are three main types of quenching: conversion, pickoff, and chemical reaction.[20]

Conversion may occur when a positronium atom collides with a molecule containing one or more unpaired electrons. In ortho-positronium, the electron undergoes a spin flip changing it into the shorter-lived para-positronium. Conversion of the singlet atom is also possible but it usually undergoes self-annihilation before it can be converted. The most common and bothersome quencher in liquids is dissolved oxygen. Care must be taken to remove it from the liquid in order to measure the positronium annihilation rates. The mechanism by which oxygen quenches and the procedure for degassing a liquid are discussed in detail in the chapter on experimental methods. Other molecules that are known to cause conversion quenching are NO, NO_2, and many of the paramagnetic transition metal cations and their complexes.

Pickoff is the annihilation of the bound positron with an electron of a colliding molecule. Again, pickoff is most noticeable for ortho-positronium and occurs when the positron part of the positronium wave function sufficiently overlaps with a singlet electron of the surrounding medium. Hence the positron "picksoff" an electron from the molecule. The ortho-positronium pickoff annihilation rate of 193 organic liquids has been measured by Grey, Sturm, and Cook.[21] They have found the average annihilation cross section, $\langle \sigma v \rangle$, to correlate directly with the electron polarizability of normal alkanes as calculated from their indicies of refraction. Partial quenching cross sections were calculated for 27 structural functional groups (See Table I) and can be used to predict molecular quenching cross sections. The average error of the calculated cross sections for 151 compounds was 1.79%. The cross sections for the remaining 42 compounds could not be calculated because they contained

Table I. Average Quenching Cross Sections.

(From Ref. 21)

	Group	$\langle\sigma v\rangle$, 10^{-14} cm^3/sec
CH_3		0.855
CH_2		0.971
CH		0.924
C		0.705
C_6H_{11}	Monosubstituted Cyclohexanes	5.515
C_6H_{10}	Disubstituted Cyclohexanes	5.373
C_5H_9	Monosubstituted Cyclopentanes	4.469
C_6H_5	Monosubstituted Benzenes	4.679
C_6H_4	Disubstituted Benzenes	4.844
-CH=CH-		1.906
CH_2=CH-		1.667
CH_2=C(CH_3)-		2.635
-CH=C(CH_3)-		3.076
H		0.129
OH		0.749
-O-	Ethers	0.836
CHO	Aldehydes	1.673
COOH	Acids	1.839
C=O	Ketones	1.786
COO-	Esters	1.939
F		0.084
Cl		1.122
Br		1.872
NH_2		1.624
$PO_3\equiv$	Phosphites	3.382
$PO_4\equiv$	Phosphates	3.754
SH	Thiols	2.330

unusual structures such as keto-enol forms or because the ortho-positronium intensity, I_2, was so small that accurate lifetime measurements could not be made.

The pickoff process in the condensed phase has been characterized by Brandt[17] using a "free volume model" in which the positronium atom is thought to occupy the interstitial volume between the molecules. The pertinent assumptions are:

(1) Mutual polarization of the lattice and the positronium is neglected.

(2) The positronium is considered to be thermalized.

(3) The lattice potential is rectangular in shape (Figure 4 gives a qualitative description of this arrangement). The potential well has height, U_o, radius, r_o corresponding to an excluded volume V_o and electron density, ρ_o. A unit cell has radius, $r_1 > r_o$ and cell volume V_1. The free volume, V^*, is equal to V_1-V_0.

The amount of free volume present in a liquid depends upon the molecular properties of the liquid, the temperature, and the pressure. Henderson and Millett[18] studied the pressure dependence of the ortho-positronium lifetime, τ_2,

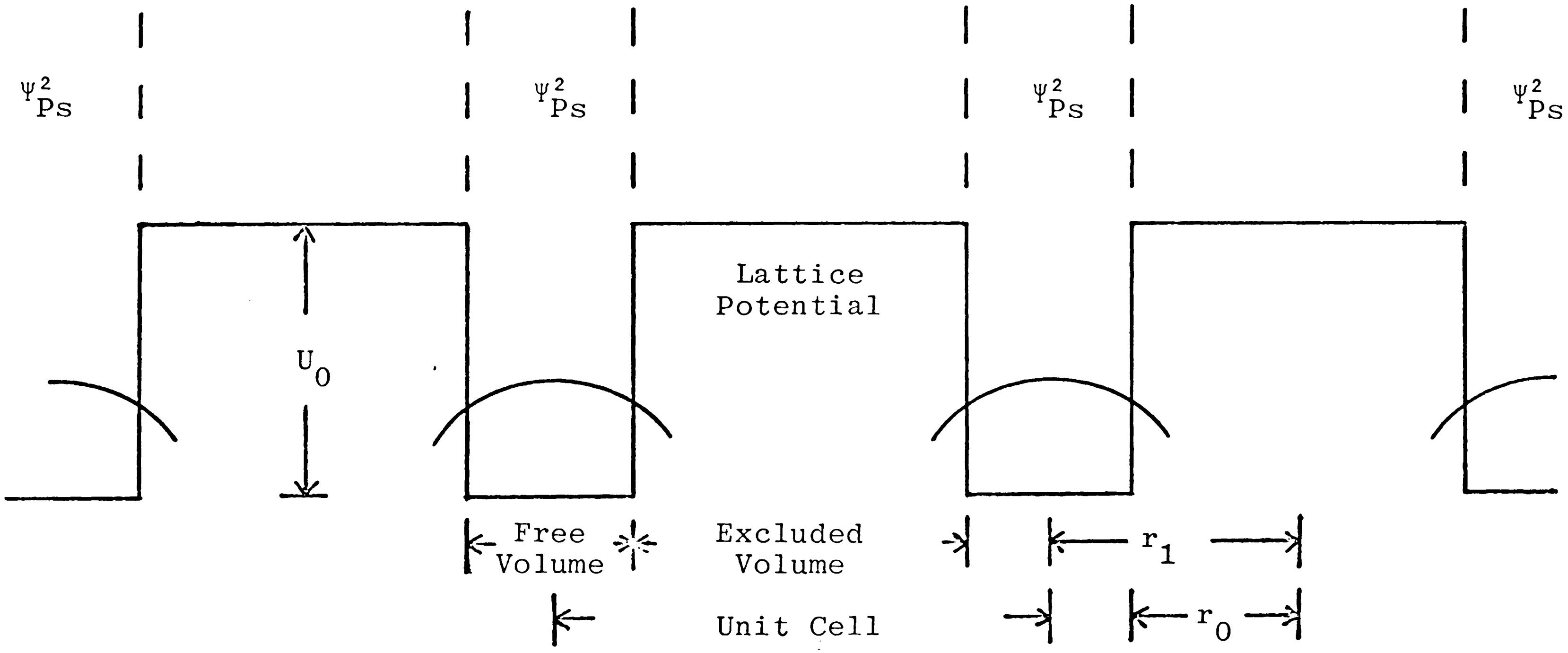


Figure 4. Lattice Potential as Described by the "Free Volume Model". (from Ref. 17)

in 22 organic liquids and established that it decreased linearly with decreasing specific volume, $V(P)/V_o$, where V_o is the volume at STP. Wilson, Johnson, and Stump[19] investigated both the temperature and pressure dependence of τ_2 in a series of liquids. They found the lifetimes to follow

$$\tau_2 = \tau_T^o \quad \exp\ (-\mu V/V_o) \qquad (13)$$

where μ is a characteristic constant for each liquid. The lifetimes of ortho-positronium in liquids that cannot be described by these relationships will be discussed in Chapter 3.

The validity of the "free volume model" is further substantiated by two photon angular correlation experiments. When singlet annihilation occurs, the two photons are emitted in exactly opposite directions, $\theta = \pi$, if the center of mass of the electron-positron pair is at rest. However, the center of mass is in motion for all practical situations and the angular distribution, $C(\theta)$ versus θ, of the annihilating photons appears bell-shaped about $\theta = \pi$ radians. The angular distribution may be used to obtain the momentum (p) distribution, $C(p)$ versus p.[22] An example of both the angular and momentum distributions is shown in Figure 5. Momentum distributions generally consist of two components. It was pointed out by Ferrell,[23] that para-

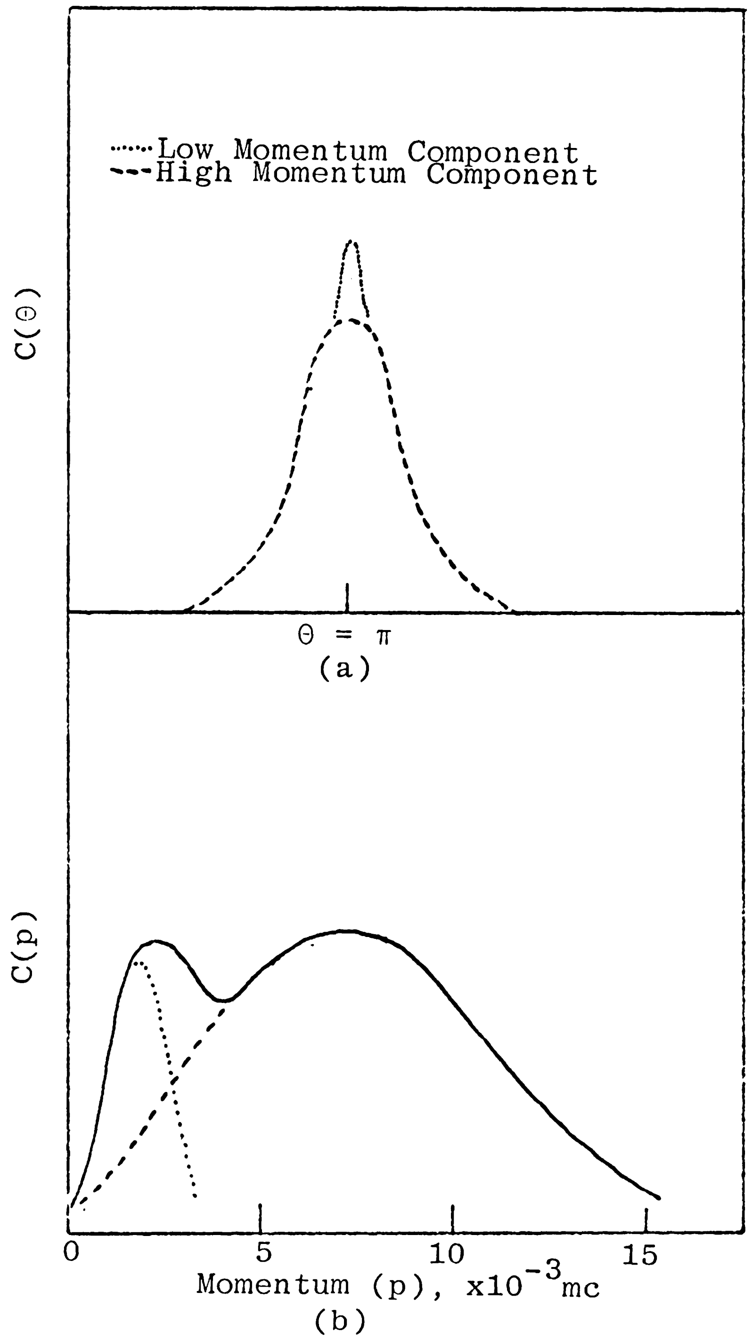


Figure 5. (a) Angular and (b) Momentum Distributions of the Annihilating Photons.

positronium should give rise to a relatively low momentum component since it usually decays by self-annihilation of the electron-positron pair. Direct positron and ortho-positronium pickoff annihilation occur with electrons bound to molecules of the system. These photons should contribute to a relatively higher momentum component because if the positron or positronium is thermalized, as is required by the bubble model, the primary contribution to the momentum of the center of mass of the annihilating pair will come from the high momentum bonding electrons. If this is true, the intensity of the low momentum component should correlate with the intensity of para-positronium as measured from lifetime measurements. Kerr *et al*[24] have compared the two intensities for ten organic liquids. The two measurements, taken from two completely different experiments, agreed within experimental error for all 10 compounds.

The higher momentum component of the momentum distribution can be used as an experimental verification of calculated electron momentum distributions if pickoff annihilation occurs as described by the "free volume model." The momentum distributions for electrons in C-C and C-H bonds have been calculated using analytic SCF functions for atomic carbon orbitals and Heitler-London-type functions for the two paired electrons in the C-C and C-H bonds.[25] The authors then computed a theoretical electron momentum distribution curve for hexane and decane. The results for decane are shown in Figure 6. Component A is approximately gaussian and corresponded to the low momentum part due to para-positronium. Component B is the calculated C-H contribution and Component C is the calculated C-C contribution. When fit to the experimental curve, the relative areas under Components B and C were found to be in the exact ratio of the electrons in the C-H bonds compared to the electrons in the C-C bonds. For hexane and decane these ratios were 28/10 and 44/18 respectively. They concluded that during pickoff annihilation, the positron of ortho-positronium annihilates primarily with the bonding electrons of a molecule.

The third kind of positronium quenching is by chemical reaction. Tao and Green[26] have divided this category into four types: (1) oxidation by electron transfer; (2) reduction; (3) compound formation; and (4) double decomposition. This thesis deals primarily with the chemical reactions by compound formation and for that reason, it will be discussed in detail in Chapter 3.

Figure 7 summarizes the many interactions of positrons and positronium in water.[20] High energy positrons lose energy rapidly while slowing down. If a collision takes place while the positron is in the Ore gap, positronium atoms are formed with excess kinetic energy. About one-

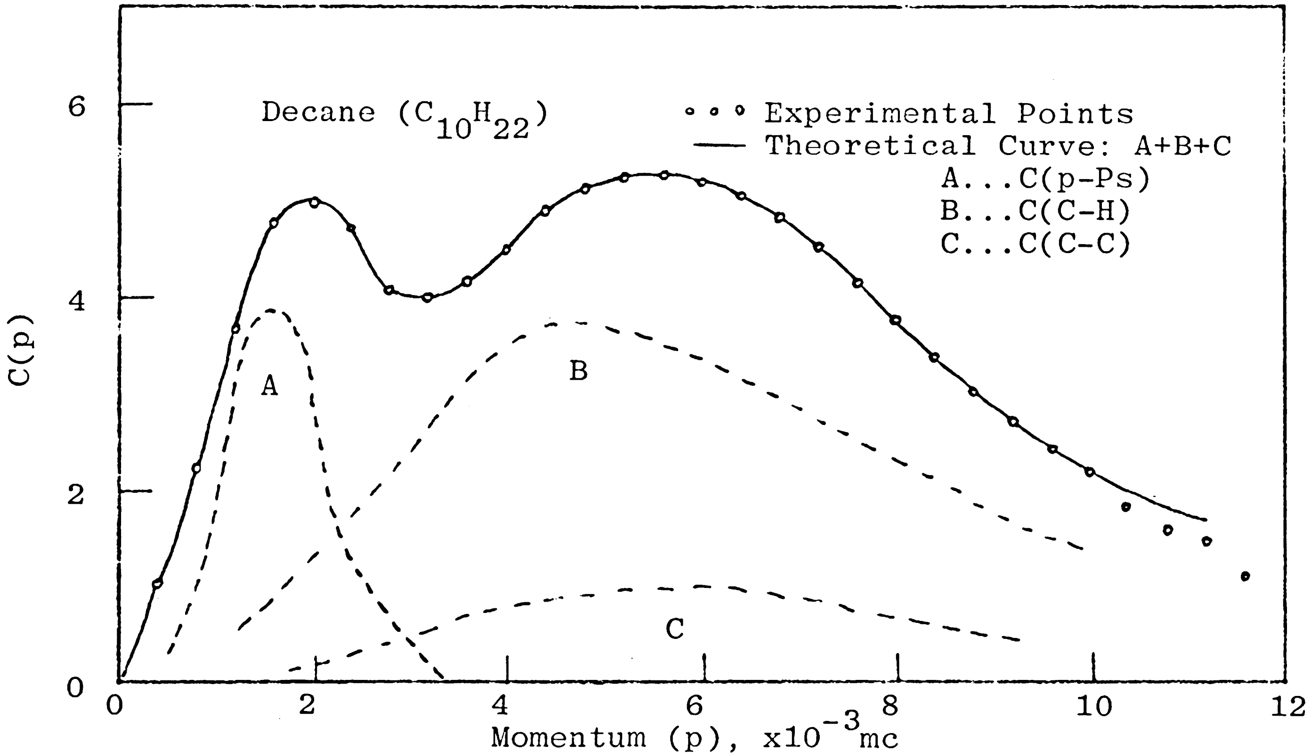


Figure 6. Computed and Experimental Momentum Distributions for Decane. (from Ref. 25)

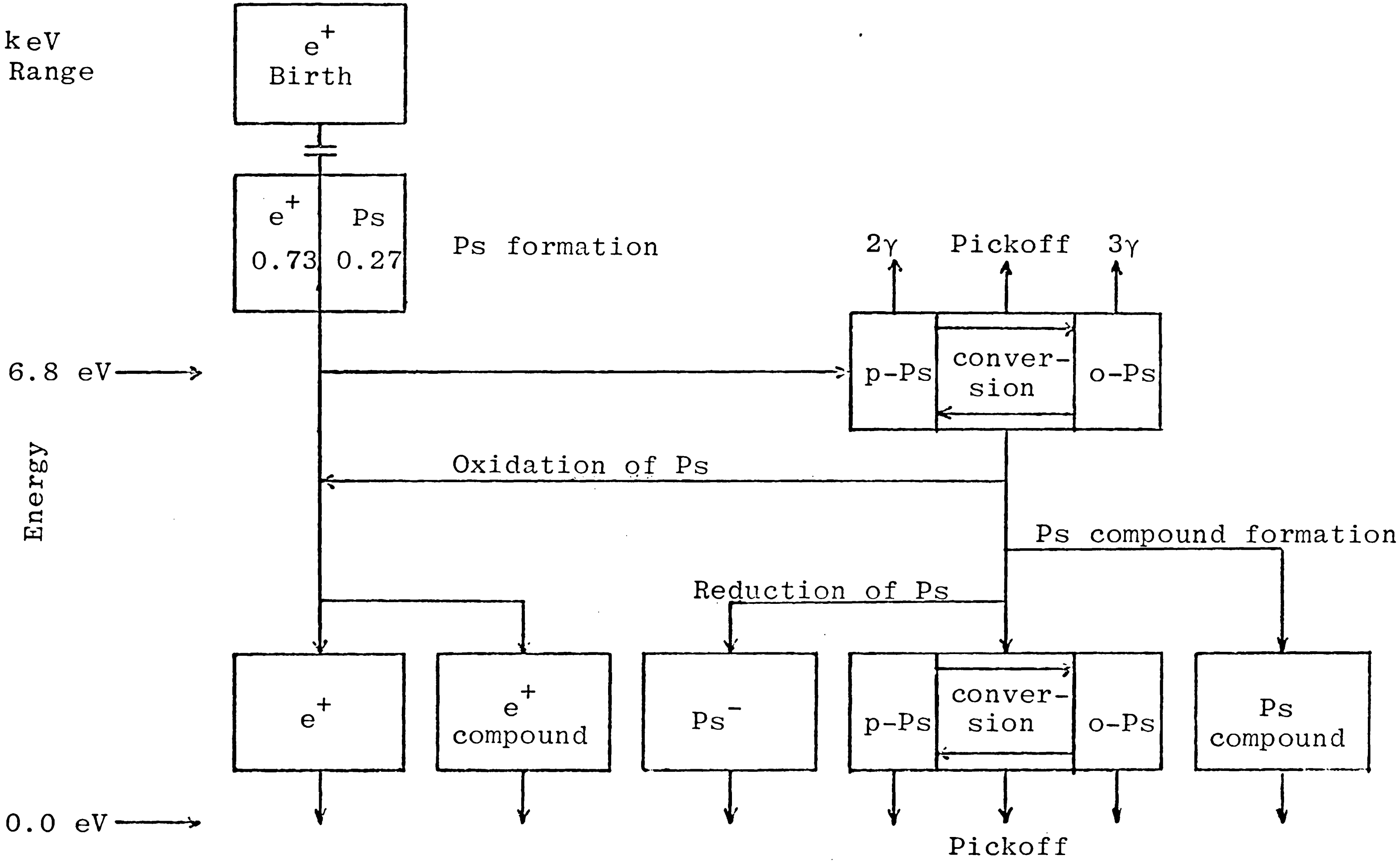


Figure 7. Positron and Positronium Decay in Water. (from Ref. 20)

third of the positrons will do this, three-fourths of them forming ortho-positronium and one-fourth forming para-positronium. If paramagnetic species are present, conversion quenching may occur. Pickoff annihilation is always possible. If strong oxidants are present, positronium may be oxidized back to a free positron. Reduction of positronium would form Ps^-, which has a binding energy of 0.3 eV, however, this species has not been observed.[8] Positronium compounds may form at any time during or after thermalization. Free positrons may annihilate or form positron complexes and then annihilate. The possibilities for interaction are numerous, some are possible only for positrons or positronium, others are analogous to the reactions of the hydrated electron or hydrogen atom, two species to which positrons and positronium are often compared.

EXPERIMENTAL METHODS

A. Introduction

Positron lifetime measurements are usually carried out by using a delayed coincidence technique.[27] This method is the most applicable one for measuring short (less than 10^{-4}s) nuclear mean lives. It requires that a start pulse be present which originates from a zero-time physical event. Also, an end-time event pulse is necessary so that both pulses can be fed into a coincidence circuit. A graph of coincidence rate plotted as a function of time is the lifetime spectrum and can be analyzed to give the lifetime of the positrons in the system. Improvements on the basic experimental arrangement were made by Bell and coworkers when they introduced the fast-slow principle[28] and the time-to-pulse-height-converter.[29]

A large majority of the data presented in this work was obtained by measuring a positron lifetime spectrum under varying conditions. These spectra were then used to measure the lifetime of free positrons as well as the lifetimes of both electron-positron bound states in solution. Positron annihilation rates are defined as the reciprocal of these positron lifetimes. These rates were used to evaluate annihilation rate constants. The measurements of certain rates as a function of temperature may be used to obtain various thermodynamic quantities. Hence, kinetic as well as thermodynamic information was obtained in order to determine the mechanism by which one of the positron species, ortho-positronium, reacted; this was a major objective of the thesis.

B. Positron Sources

In the study of positronium chemistry, the most widely used source of positrons is sodium-22 which has a half-life of 2.60 years. It may be purchased from some of the major radionuclide distributors either as carrier free $^{22}NaCl$, $^{22}NaHCO_3$, or as carrier solutions of these compounds. The decay scheme[30] of ^{22}Na is shown in Fig. 8. A majority of the decays (90%) cause positron emission and leave the daughter nuclei, neon-22, in a very short lived (τ = 3psec) excited state. Electron capture (EC) decay, in which no positron is formed, occurs ten percent of the time. The ground state of sodium-22 lies 2.840 MeV above the ground state of neon-22 and 1.564 MeV above the first excited state of neon-22. However, the maximum positron energy is only 0.544 MeV due to the energy requirements placed upon positron decay as explained in Chapter 1. The transition from the first excited state of neon-22 to its ground state takes place in a time two to three orders of magnitude faster than the average lifetime of a positron in condensed matter. Consequently, the 1.276 MeV gamma-ray can be used to initiate the zero-time start pulse required for coinci-

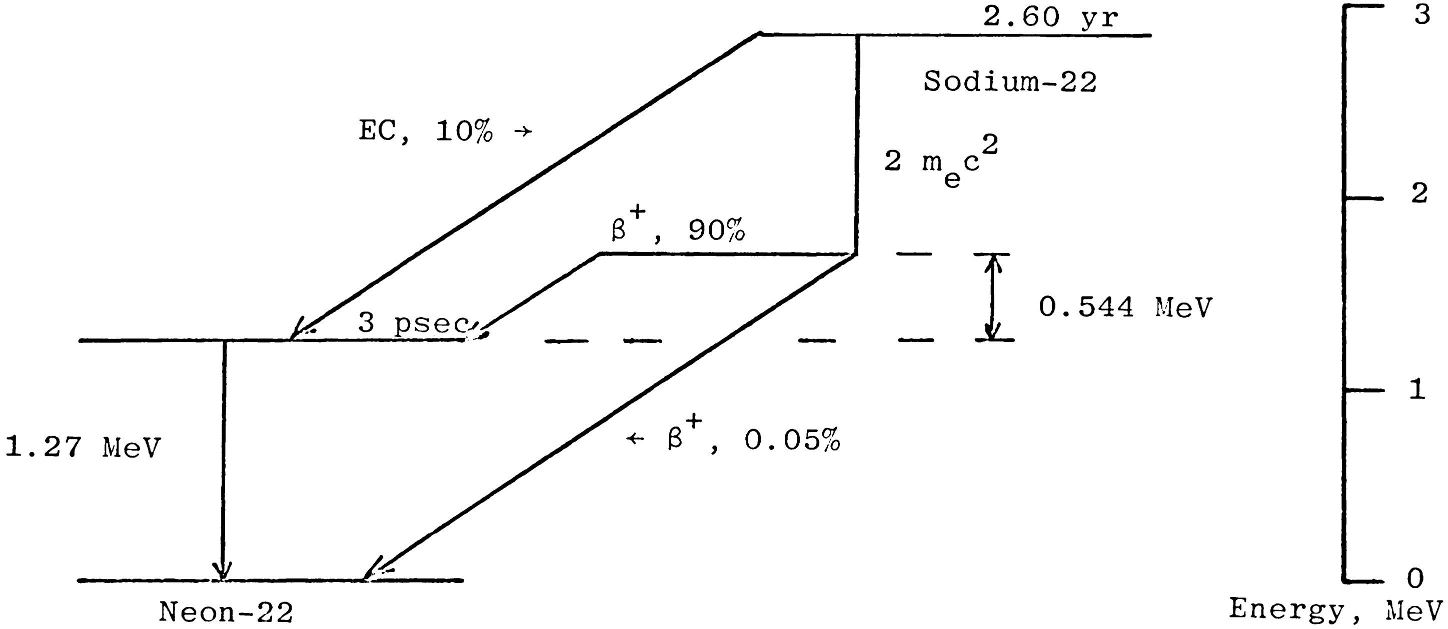


Figure 8. Decay Scheme of Sodium-22. (from Ref. 30)

dence studies, and the annihilation gamma rays used for the end-time signal.

All of the data presented in this study were taken on positrons annihilating in the liquid phase. The solid support for the positron source was a 1 mil thick aluminum foil, 5 mm by 10 mm in size. A water solution containing the sodium-22 was added dropwise to the foil and evaporated at atmospheric pressure under an incandescent lamp. This procedure was repeated until the foil contained the desired activity. This rather arbitrary amount of activity depended upon the specific activity of the sodium-22 solution, the number of drops added and the counting efficiency of the detector system. Ideally, one tried to place enough activity on the foil so that a spectrum containing at least 15,000 counts in the peak channel could be obtained every six to eight hours. In working with most organic liquids, the solubility of the sodium-22 compounds was small and very little activity was lost from the foil during the course of the experiment.

Activity losses due to the degassing procedure will be discussed in the sample preparation and degassing section of this chapter. Positron annihilation in the aluminum foil and Pyrex glass sample tubes has been studied[31] and found not to be a problem when using the abovementioned procedures.

C. Fast-Slow Delayed Coincidence Counting

A typical arrangement for a fast-slow coincidence timing system is shown in Figure 9. A fraction of the gamma photons emitted during the positron decay and annihilation processes in the source are stopped by the two plastic scintillators (phosphors). Each unit consists of a phosphor optically coupled to a photo-multiplier (PHOTO-MULT) tube. The phosphors used were Nation 156 plastic scintillators, 1" by 1". They have a fast decay constant in comparison to the positron lifetimes and also high light output. The photomultiplier tubes were RCA 8575 mounted on Ortec 265 photomultiplier bases (PM BASE). They were used for their high gain, fast rise time, and are low in the emission of thermal electrons. The output signals from these detectors are simultaneously fed into two coupled electronic circuits. The circuits consist of a fast inner loop and a slow outer loop. Each circuit has two sides, a start side and a stop side.

The inner circuit was used to accurately determine the time interval between the formation of the positron and its subsequent decay. The output from the anode of the detector is sent to an Ortec 417 fast discriminator (FAST DISC). The units are operated at a biased voltage in order to reduce the noise level in the circuit by setting a lower threshold limit for accepting pulses from the photomultiplier tube. Both fast discriminators send out fast timing pulses to an Ortec

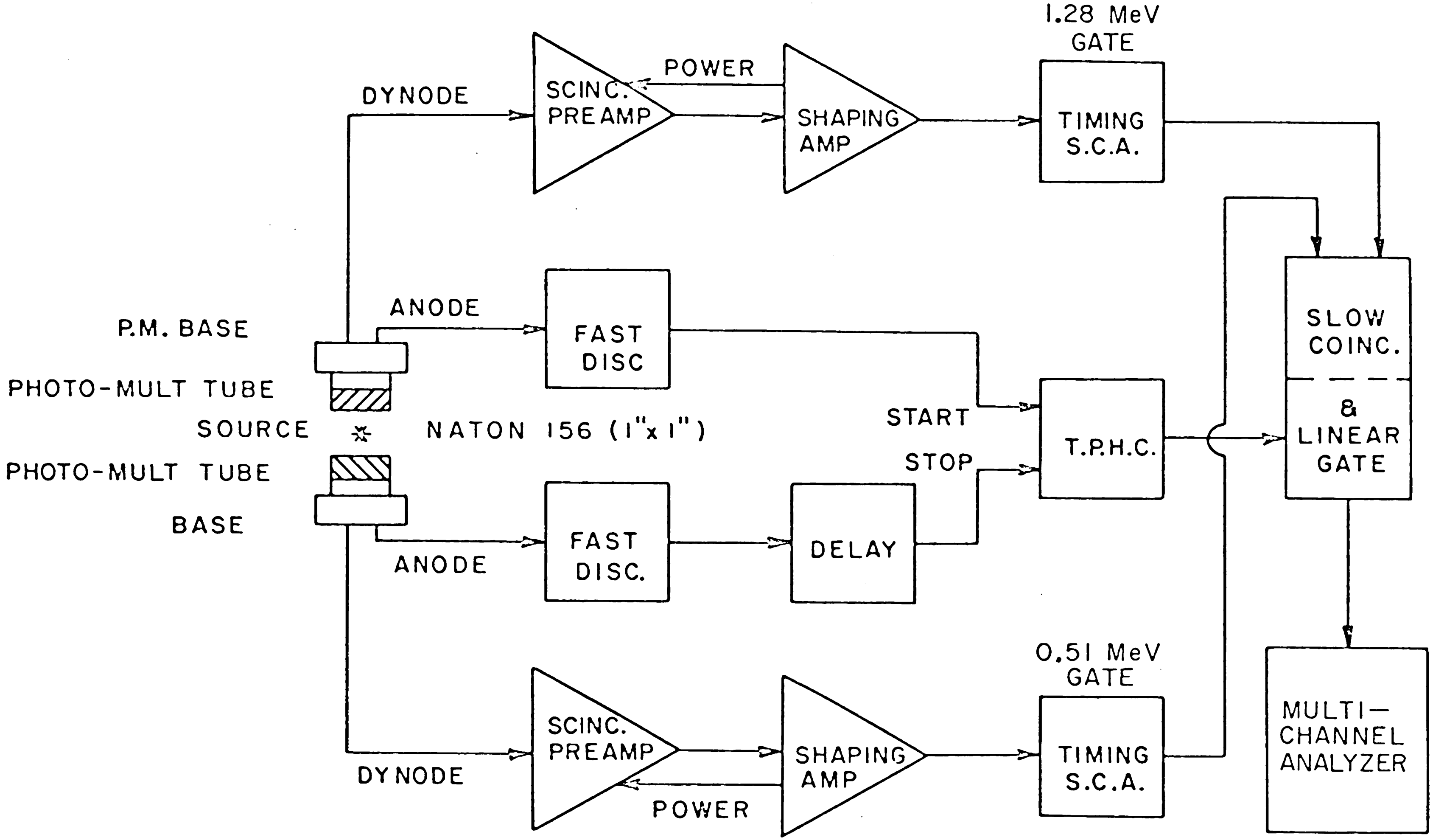


Figure 9. Simple Fast-Slow Timing System.

437 time-to-pulse-height-converter (TPHC). This unit converts the time difference between the start and stop pulses into a proportional pulse height signal. Before this pulse is allowed to pass into the multichannel analyzer (MCA), certain energy and coincidence conditions must be met. An Ortec 425 variable delay unit is inserted into the fast circuit to calibrate the channel width, time increment per channel, of the multichannel analyzer. The calibration procedure and the importance of this quantity will be discussed later.

The outer or slow loop takes its signals from the dynodes of the photomultiplier tubes. These signals have not been fully amplified in the detectors and therefore must first be amplified and shaped by means of an Ortec 113 scintillation preamplifier (SCINT PREAMP) and then an Ortec 440 shaping amplifier (AMP). Both sides of the slow circuit contain an Ortec 420 timing single channel analyzer (TIMING SCA). On the start side, this unit is biased so that an energy window is created that will only accept pulses that correspond in energy to very nearly 1.276 MeV. This is the energy of the de-excitation photon emitted during positron decay. Pulses substantially larger or smaller than this are rejected by the unit. The timing single channel analyzer in the stop side of this circuit performs the very same function for 0.511 MeV pulses, those from the annihilation process. If both the start and stop pulses reach the Ortec 409 slow coincidence (COINC) and linear gate unit (this time is called the resolving time and is usually less than a μs) within a short time interval, the slow coincidence unit opens the linear gate and the signal from the time-to-pulse-height converter is allowed to pass into the multichannel analyzer. Overall, three different multichannel analyzers were used in this study. They were a Nuclear Data 2200, a Northern 600, and a Packard. They were all operated in a pulse height analysis (PHA) mode. These units will accept pulses of varying heights and sort them accordingly. These data representing the lifetime distribution are stored in the memory and can be read-out of the units in hard copy form onto paper, paper tape, or magnetic tape. Once the lifetime distribution data are taken out of the memory, it can then be computer analyzed into its various lifetime components.

The positron lifetime measurement begins when the starting detector accepts the zero-time pulse corresponding to the emission of a position and continues until the end-time pulse from the decay of that positron is received. The lifetime of that positron is stored in memory and the coincidence circuits are cleared in order to measure the lifetime of another positron, etc. This procedure is analogous to having a large number of positrons at time t=o and observing their lifetime distribution.

D. Positron Lifetime Spectra

The end result of the experiment described in the previous section is a positron lifetime spectrum. A typical spectrum is shown in Fig. 10. The ordinate of Fig. 10 gives the logarithm of the number of two-gamma decays while the abscissa is the time axis in nanosecond units. A point on the curve, (log N(t), t), represents the number of positrons that have lived for a certain time t and then decayed by two-gamma emission. This two component exponential decay spectrum is typical of positrons decaying in a condensed phase. The steeper short-lived component, λ_1, is attributed to the decay of free positrons, those which have not formed a bound state with an electron, and para-positronium, the singlet bound state. The more shallow long-lived component, λ_2, is assigned to ortho-positronium. Even though this species lives in solution as a triplet, its positron annihilates with a singlet electron by two-gamma emission before it reaches its expected lifetime.

In general, a multicomponent exponential decay spectrum has the following form.

$$N(t) = \sum_i N_i \exp(-\lambda_i t) + \text{background}$$

where the N_i's are the pre-exponential constants that weight the individual components, and the λ_i's are the annihilation rates for the various modes of positron decay. A mean life,

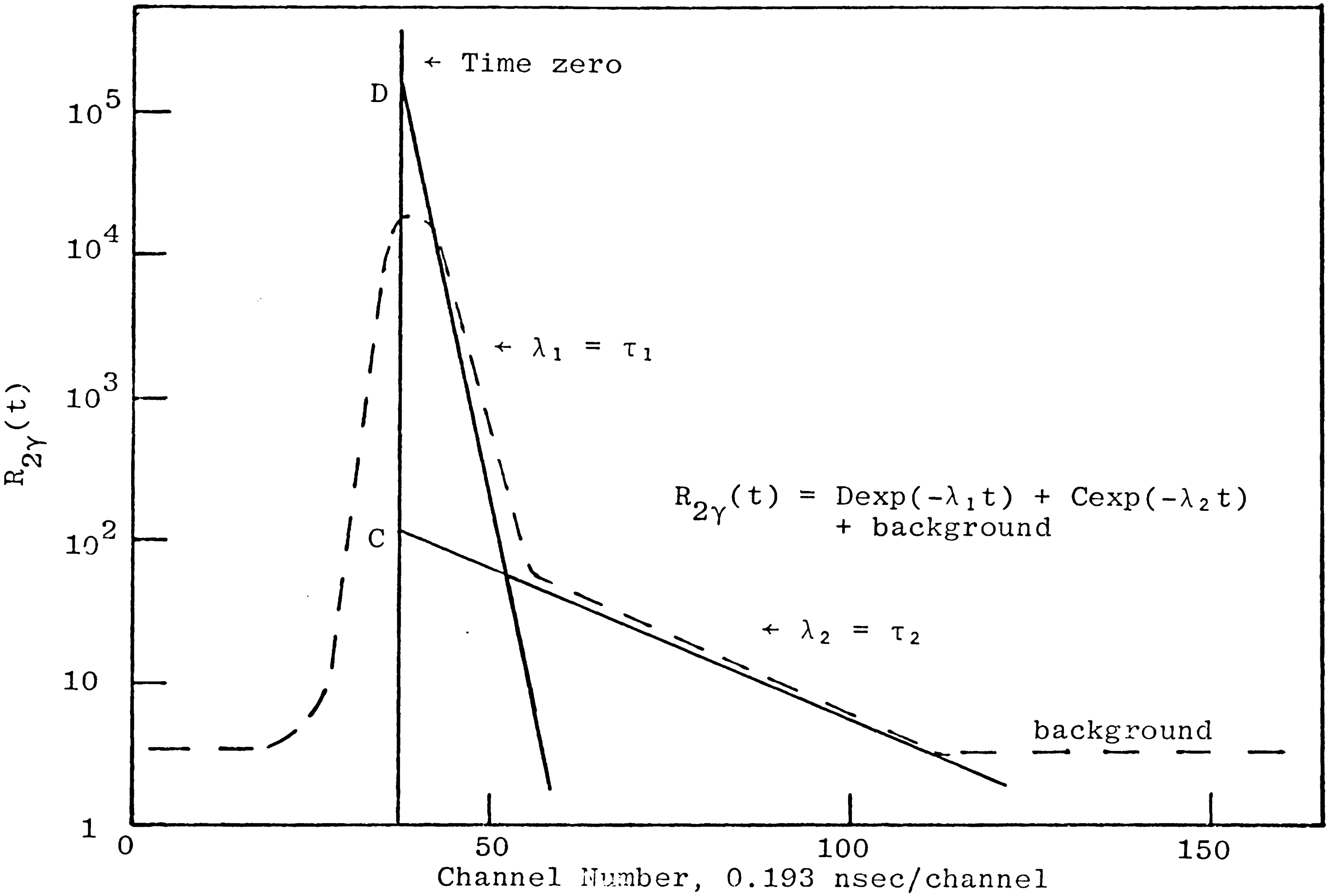


Figure 10. Typical Positron Lifetime Spectrum.

τ_i, is shown as the reciprocal of the i<u>th</u> annihilation rate. These spectra can be computer resolved into their various components using programs originally written by Cumming[32] or Tao[33] and then modified in this laboratory. The programs were run on the IBM 360/155 computer located at the Virginia Tech Computing Center. Briefly, the programs perform a linear least squares analysis on each component present in the spectrum starting with the longest lived one and then constructs a calculated spectrum. The lifetime, annihilation rate, and intensity of each component is output along with a calculated fit parameter. This fit is a rather complicated function of the standard deviation and values less than 2.00 are generally acceptable. In addition to the printer output is a Calcomp plot of the experimental data and the calculated spectrum which can be obtained by using the PAL program.[34] An example of the Calcomp plot is given by Fig. 11.

This is a plot of the base ten logarithm of the coincidence rate versus time. The calculated fit is 1.05. The calculated lifetime and intensity of the two components are τ_1 = 0.398 nsec, I_1 = 80.4% and τ_2 = 2.162 nsec, I_2 = 19.6%. The PAL program requires that the calculation be started beyond the curved top of the peak at a point where the first component appears to decay linearly. This distortion at the peak is caused by the finite resolving power of the instrument and will be discussed later. The total area under the

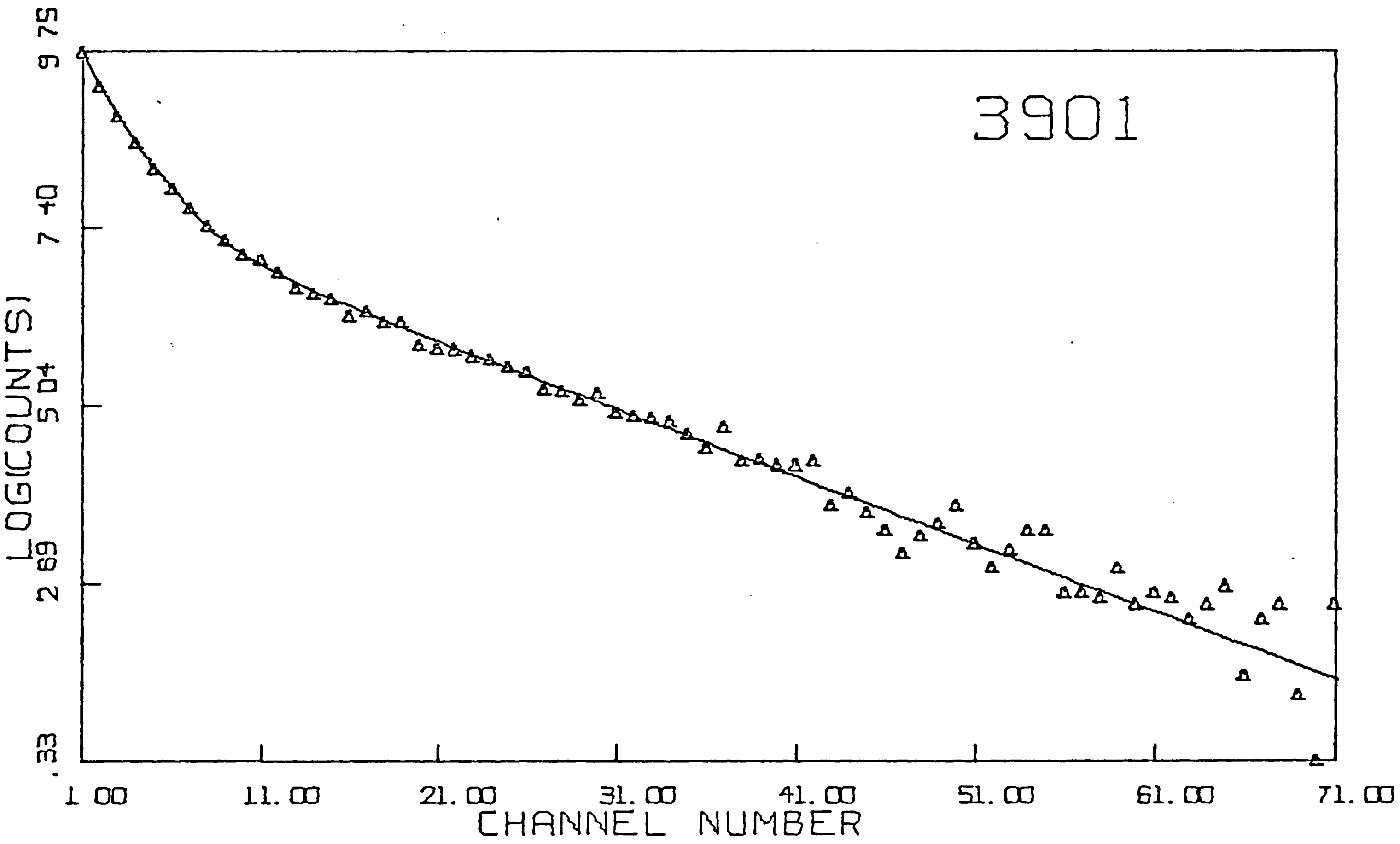


Figure 11. Typical Calcomp Plot of the Lifetime Data.

two components is normalized by the program to 100% so that by reporting the intensity of either component, one automatically sets the intensity of the other. No such relationship can be applied to the annihilation rates, however λ_1 remains fairly constant at 2.5 ns^{-1} in the liquid phase and, therefore, will not be reported here. It is λ_2, the annihilation rate of ortho-positronium and its intensity, I_2, that have been shown to be of interest chemically.[35] A quantity that is used to evaluate the ability of any fast-slow coincidence unit to resolve a multicomponent spectrum is termed the resolution of such a unit. This parameter has time units and is defined as the full-width-at-half-maximum (FWHM) of a prompt spectrum. A prompt spectrum is one in which the zero-time and end-time pulses are received by the detectors simultaneously. Ideally, a single spike should be seen in the lifetime spectrum corresponding to time t=o. Experimentally, this can easily be done by placing a cobalt-60 source between the two detectors. Cobalt-60 decays by negatron emission and emits a 1.173 and a 1.333 MeV gamma ray coincidently. If the two timing single channel analyzers are set so that these two photons are used to start and stop the timing measurement, a prompt spectrum can be obtained. Due to the inadequate time resolution of the instrument, the prompt spectrum appears broadened about t=o as shown in Fig. 12. The resolution, FWHM, was typically 300-400 psec for the experiments reported here.

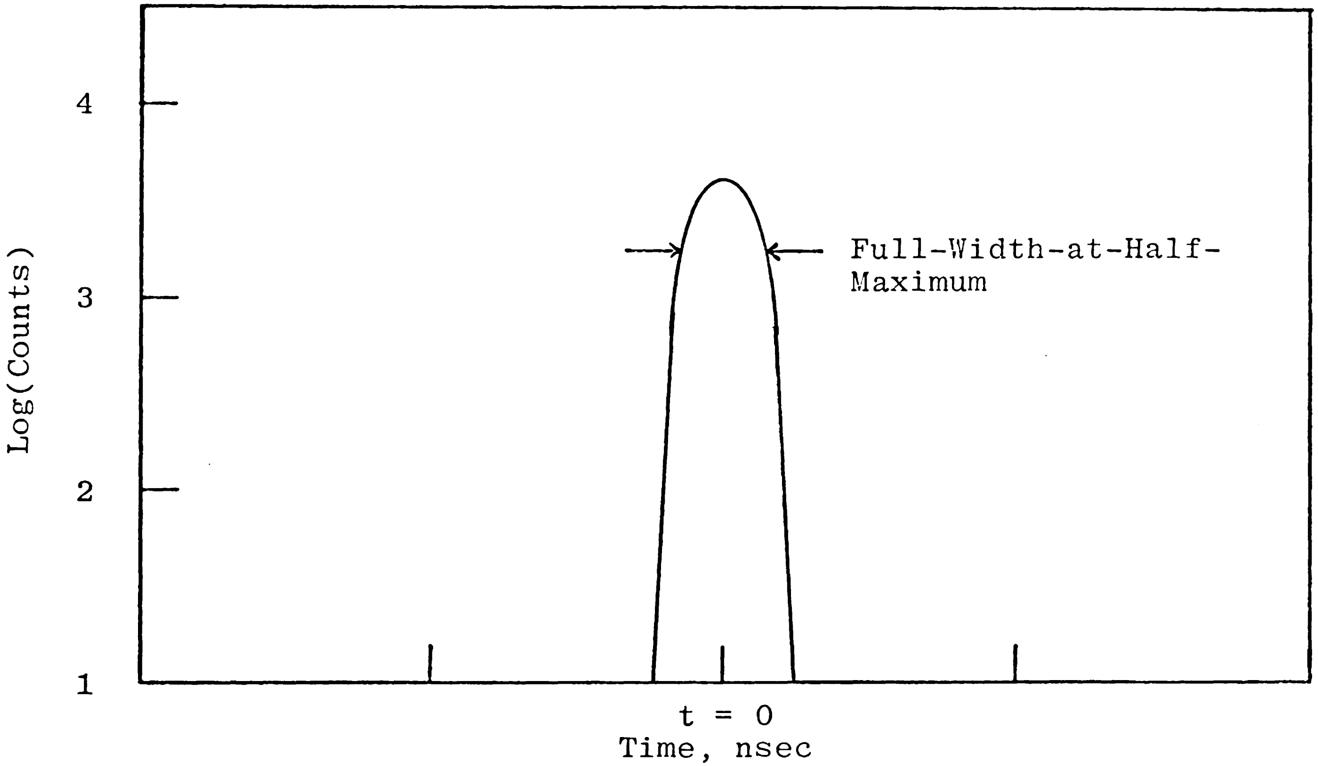


Figure 12. Prompt Spectrum of Cobalt-60.

By inserting a known delay, i.e. 16 nsec, into the timing circuit of Fig. 9, the prompt spectrum can be moved 16 nsec down the time axis. The number of channels between the maximum of the prompt spectrum with no delay and the maximum of the prompt spectrum with a 16 nsec delay can then be used to calibrate the channel width, time increment per channel. For this work, a 16 nsec delay caused the prompt maximum to move 83 channels which represents a channel width of 0.193 nsec/channel. This parameter is essential for accurately evaluating the individual components (slopes) of the lifetime spectrum and has been checked regularly.

E. Sample Preparation and Degassing

Measuring the positron lifetime distribution in the liquid phase requires a sample vial capable of holding the aluminum foil positron source and a few milliliters of solution. The vial has been constructed so that its contents could be easily degassed.

The rate constants for the reactions of ortho-positronium were calculated by measuring the ortho-positronium annihilation rates at various concentrations of the reactive compounds. The sample tube used in this type of experiment is shown in Fig. 13. It was constructed of cylindircal Pyrex glass tubing, approximately 200 mm long, 10 mm i.d. at the narrow counting end, and 25 mm i.d. at the top.

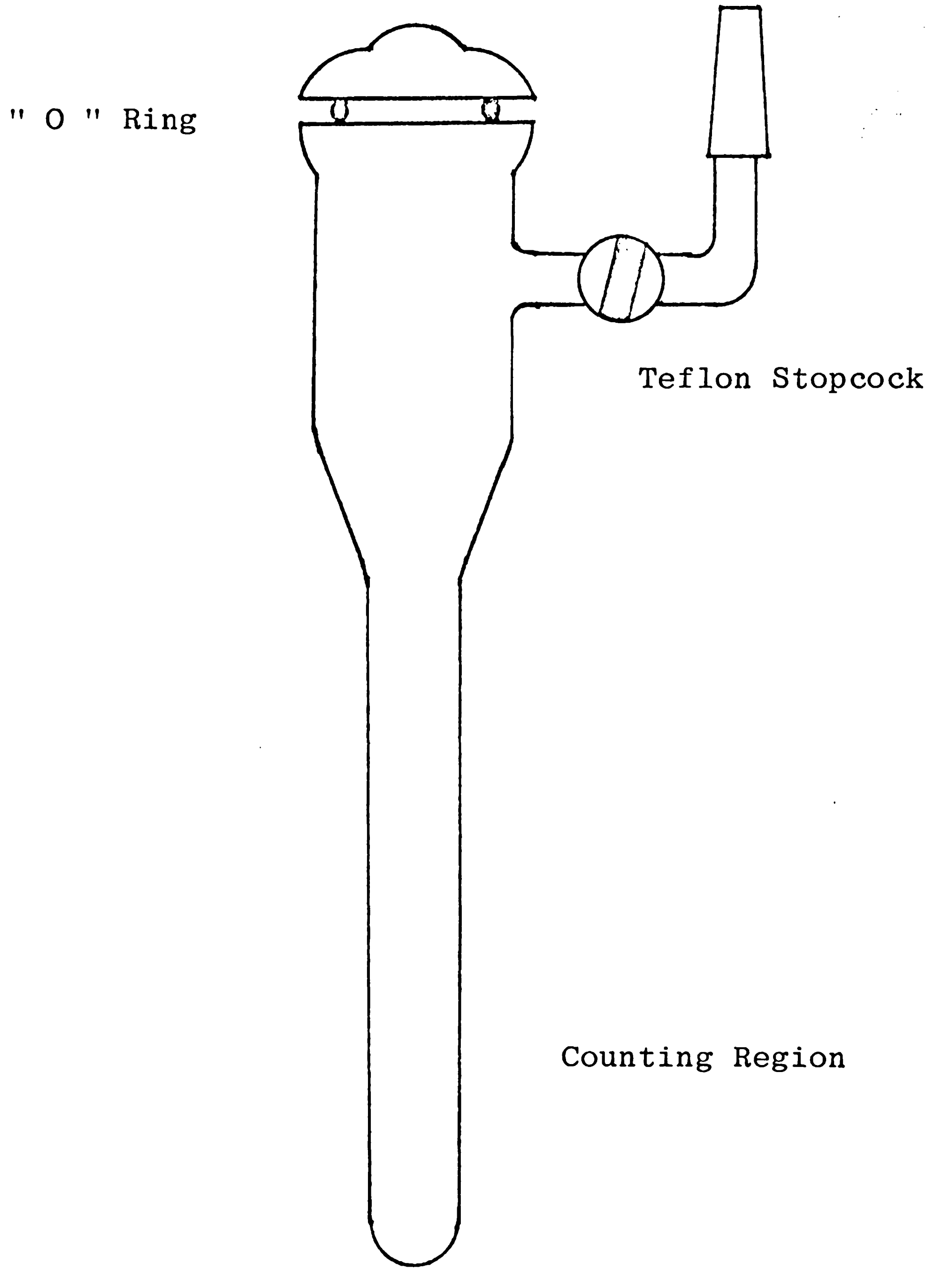


Figure 13. Sample Tube used for Variable Concentration Experiments.

Perkal[31] has shown that a positron in a liquid such as water will travel approximately 0.5 mm before annihilating. A right angle side arm with Teflon stopcock was fitted to the wider portion and a mole 10/40 ground glass joint was attached so that the sample tube could be connected to the vacuum manifold. The lid was sealed to the main body of the tube by a Teflon "O" ring and held by a clamp (not shown). This arrangement has only been used for lifetime measurements taken at room temperature.

For measuring annihilation rates at temperatures above and below 295°K, a special sample tube was used. The degassing bulb and sample tube for this type of measurement are shown in Fig. 14. The sample tube was a Pyrex glass tube about 100 mm long and 10 mm i.d. at the bottom. It was tapered to a capillary and had a male 10/40 ground glass joint on top. The wide bottom portion was broken so that the aluminum foil positron source could be inserted and then it was resealed. The solution to be counted, about 2 ml, was introduced via a capillary syringe through the top. The tube containing the source and solution was then fitted into the female 10/20 joint of the degassing bulb. The male joint of the sample tube protruded past the end of the female joint of the bulb by approximately 8 mm (see dotted line in Fig. 14). This prevented the solution that splashed up into the bulb during degassing from becoming

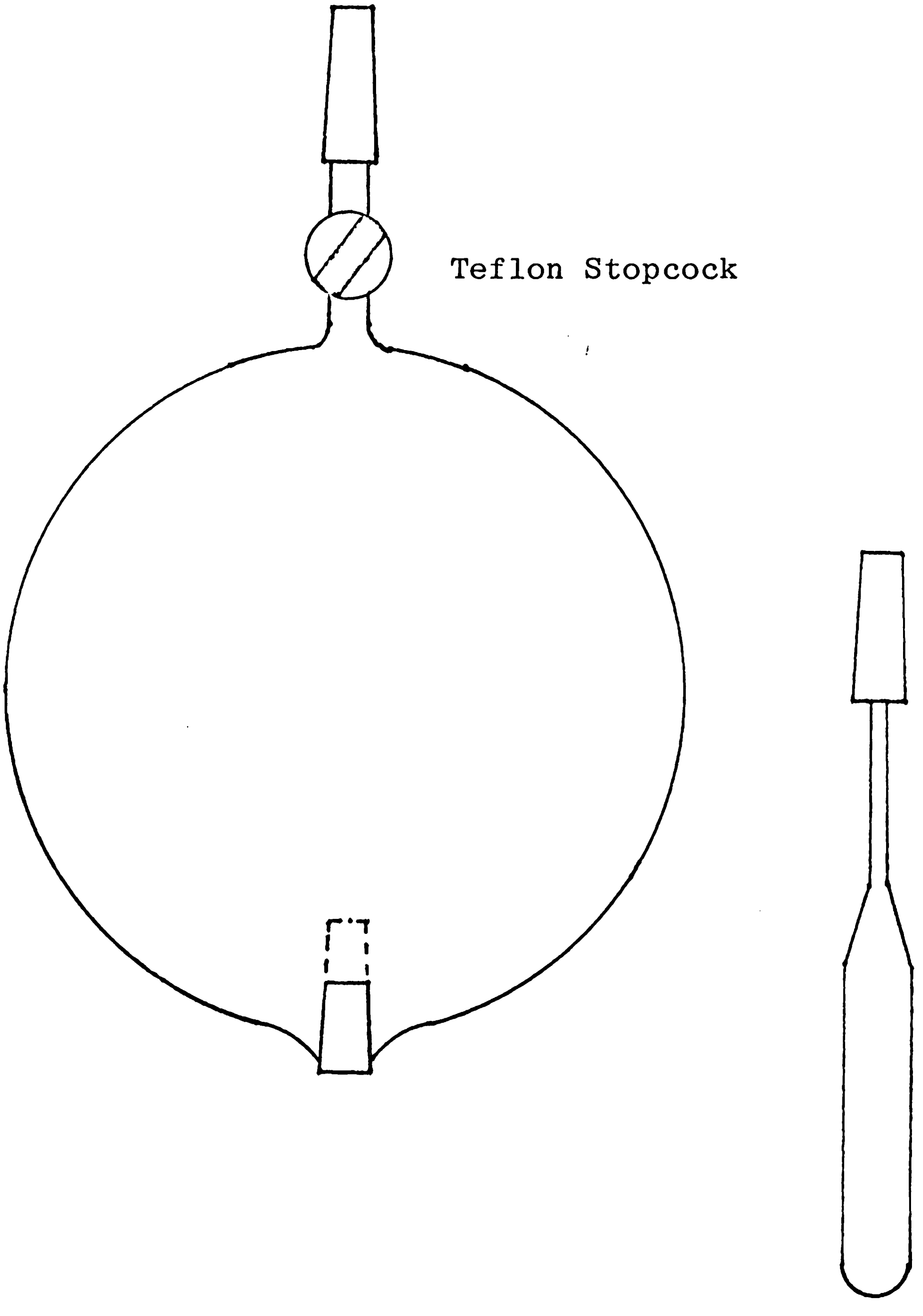


Figure 14. Degassing Bulb and Sample Tube used for Variable Temperature Experiments.

contaminated by the stopcock grease and running back into the sample tube. The degassing bulb was 75 mm in diameter, contained a Teflon stopcock to isolate the sample from the vacuum, and was fitted with male 10/40 ground glass joint for attaching it to the vacuum manifold. This relatively easy design proved quite adequate.

In dealing with organic liquids, the presence of dissolved oxygen drastically reduces τ_2. This was first shown by Lee and Celitans[36] in 1966 and later by Cooper *et al*[37] in 1967. Even today, data that was taken in the presence of dissolved oxygen is still appearing in the literature and must be discounted. The process responsible for the shortening of the ortho-positronium lifetime has been found to be conversion quenching.[38] Arguments are made indicating that the triplet ortho-positronium reacts with the unpaired electrons of the oxygen molecules in such a way that the electron of the positronium atom is caused to spin-flip creating the much shorter lived para-positronium. In order to remove this quencher, each sample must be thoroughly degassed by a simple freeze-thaw technique. The sample tube is attached to the vacuum manifold and the section containing the solution is frozen by liquid nitrogen to avoid any evaporation losses. The Teflon stopcock is opened and the vial is evacuated to 10^{-4} torr using an oil diffusion pump. The stopcock is then closed and the frozen sample is allowed to come to room temperature. This allows the dissolved oxygen to equilibrate between the solution and the partial vacuum above it. The sample is then refrozen, the stopcock opened and the oxygen above the frozen sample is pumped off. This procedure should be repeated 5-7 times or until the solution no longer is seen to give off bubbles upon thawing. For the variable concentration studies, the sample tube requires no further preparation and can be counted immediately after degassing. For the variable temperature studies, the sample must still be sealed at the capillary. So, after the last degassing, the sample was refrozen, the stopcock opened, and the capillary heated with a propane torch so that the capillary collapsed under the reduced pressure and the sealed sample tube removed from its ground glass joint.

Repeated degassing causes the aluminum foil backing to become brittle. When this occurs, the activity can be removed by dissolving the sodium-22 compound in water and then discarding the foil. The recovered activity can be reused. The degassing process also causes some activity to be worn off of the source. This will appear as a slower counting rate each time the source is used. It cannot be avoided and more activity must be added to the source periodically.

The counting room temperature was maintained at 22°C (295°K) and no special temperature regulation was used for the variable concentration studies. Measurements below room temperature were carried out in a Dewar flask fitted with a cold finger as shown in Fig. 15. The sealed cylindrical sample tube is fastened to a glass rod by a piece of rubber tubing and the temperature is measured by a Fisher low temperature thermometer. A variety of low temperature liquid nitrogen[39] slush baths were used along with isopropanol/dry ice (-75°C) and water/ice (4°C) baths. The Dewar was filled with the coolant and the cold finger placed between the two detectors for counting.

Temperatures above room temperature were maintained by the thermostated oil bath shown in Fig. 16. The oil, Fisher oil bath oil, was stirred by a magnetic stirring bar and insulated by the Dewar flask. The sample tube, thermometer, and platinum heating coil were submerged in the oil. The heating coil current was controlled by two thermistors and regulated by an external potentiometer. The apparatus was capable of reaching 220 (±2)°C.

F. Solvents and Solutes

The solvents used in this study were benzene, toluene, n-heptane, and n-pentanol. Benzene and toluene were both Fisher Spectroanalyzed, the n-pentanol was Fisher Research Grade, and the n-heptane was Phillips Research Grade. All

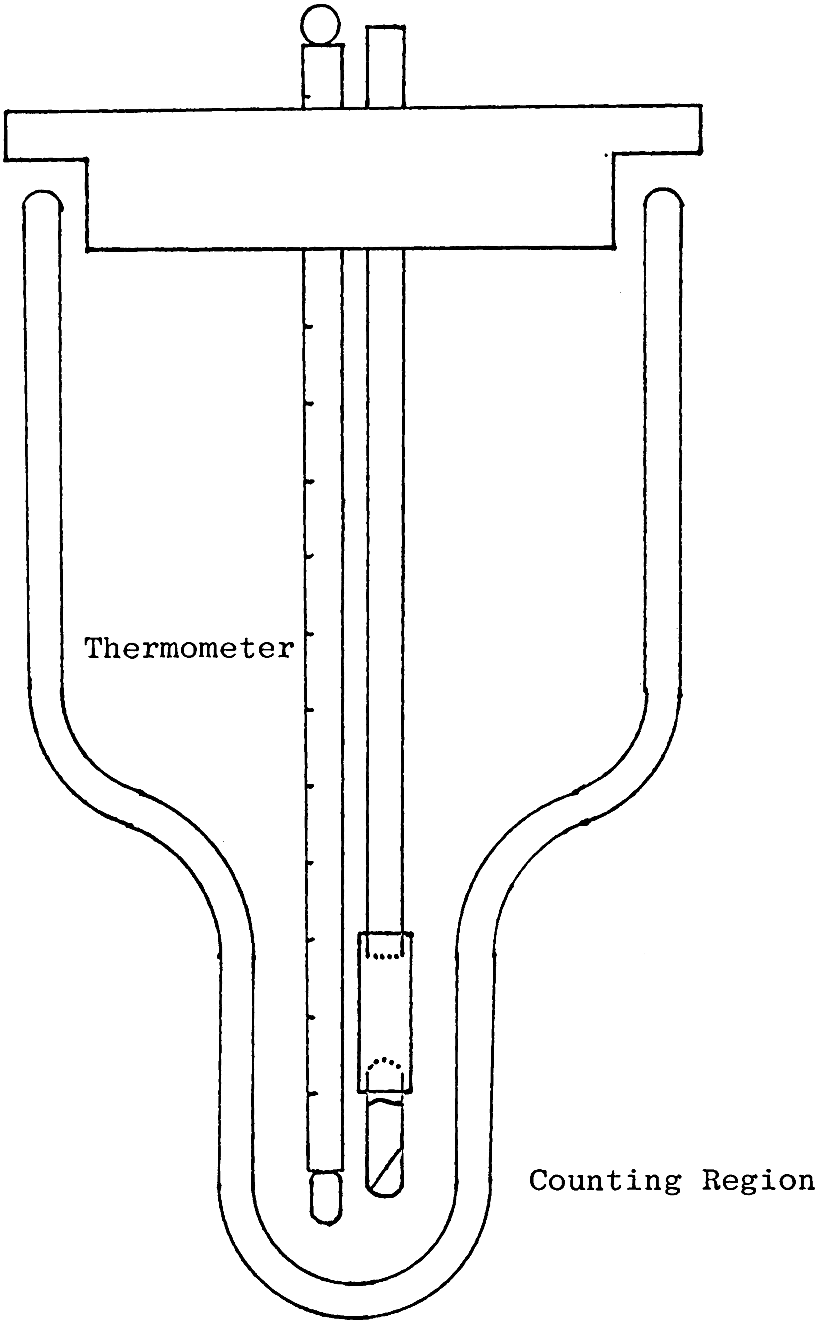


Figure 15. Experimental Arrangement used for Low Temperature Lifetime Measurements.

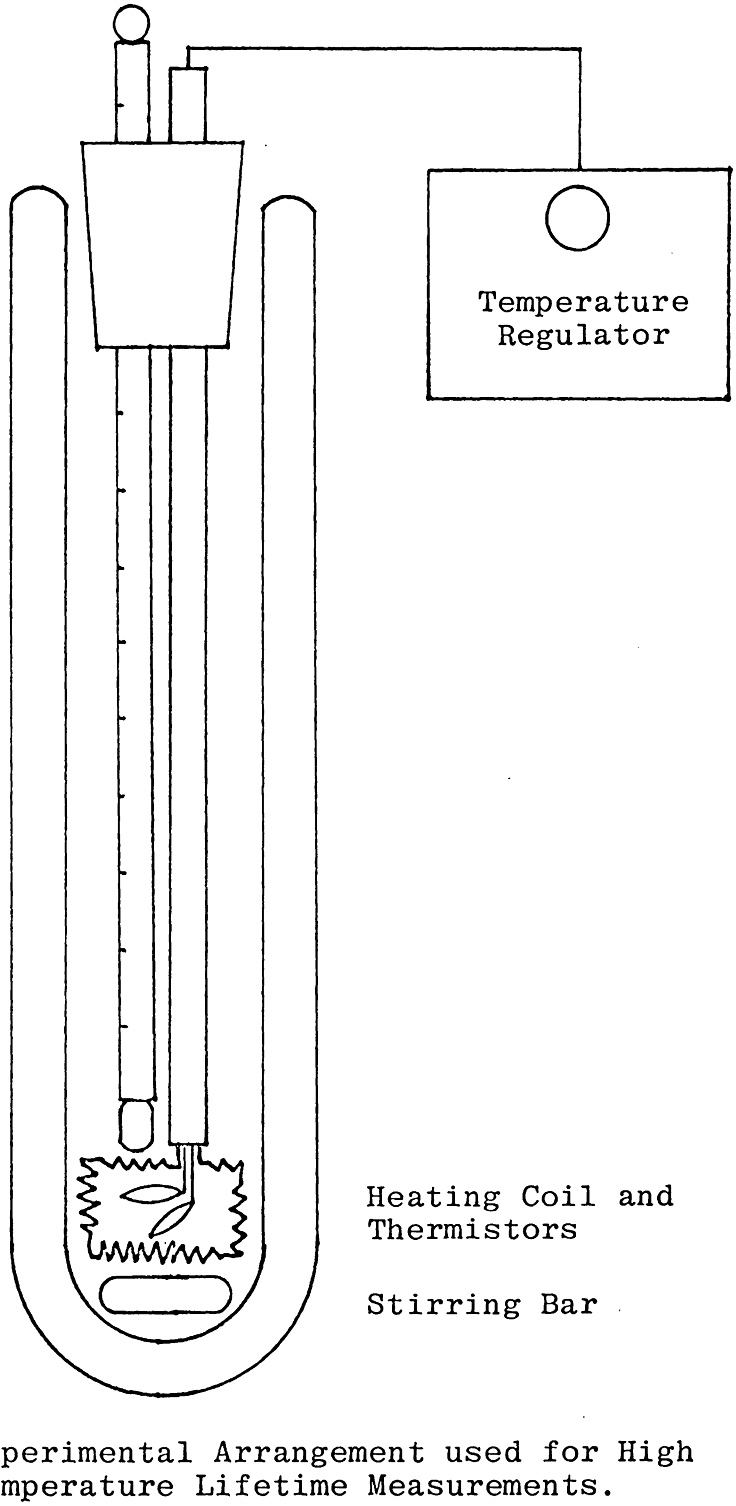


Figure 16. Experimental Arrangement used for High Temperature Lifetime Measurements.

were used without further purification; however, molecular sieve material was added to remove dissolved water.

The organic nitro compounds are all obtainable from Aldrich Chemical Company and were of the highest purity available. Most solids were recrystallized and most liquids were distilled until their melting points or refractive indicies agreed with handbook values.

CHEMICAL REACTIONS OF ORTHO-POSITRONIUM

A. Diamagnetic Quenchers

There are certain diamagnetic compounds that are able to quench the lifetime of ortho-positronium to such an extent that the long-lived component of the positron lifetime spectrum is absent. Among them are the nitroaromatics, quinones, certain compounds that resemble maleic anhydride in structure and composition and some nitriles. Goldanskii[40,41] was the first to observe this behavior in dilute solutions of nitrobenzene in benzene.

If the ortho-positronium lifetime is shortened so that it becomes indistinguishable with the lifetimes of free positrons and para-positronium, then the positron lifetime spectrum appears as a rapidly decaying one-component exponential decay curve. This is thought to be caused by rapid chemical reaction of the ortho-positronium. The ortho-positronium annihilation rate, the one that gives rise to the shallow component in the spectrum, increased to such an extent that the long-lived component was "pushed" into the shorter-lived steep one. However, inhibition of positronium formation will also cause the long-lived component to be absent from the spectrum. If ortho-positronium is not formed in any significant amount, $I_2 \approx 0$ and the long-lived component "drop out" of the spectrum.

It is rather simple to determine whether inhibition of positronium formation or rapid chemical reaction is taking place. The lifetime spectrum is observed as a function of increasing solute concentration in a suitable solvent. One that will give both a long-lived second component, $\tau_2 > 2$ nsec, and a fairly high second component intensity, $I_2 > 20\%$. (These values should serve only as general guidelines). Positronium atoms that react while still possessing a considerable amount of kinetic energy must do so very early in their lifetimes and annihilations by this mode appear in the short-lived component. If on the other hand, the annihilation rate remains constant but I_2 decreases from the value in the pure solvent, I_2^o, to zero, inhibition of ortho-positronium formation is occurring. Goldanskii[41] proposed the following mechanism for the reaction of ortho-positronium with nitrobenzene and other rapidly reacting compounds.

$$\begin{tikzcd} & & M^- + e^+ \arrow[r] & 2\gamma \\ Ps + M \arrow[r, "k"] & PsM \arrow[ur] \arrow[dr] & & \\ & & M + 2\gamma & \end{tikzcd} \qquad (1)$$

The positronium atom is thought to form a complex with the reacting molecule, M, and either annihilate while in the complex (lower path) or, since all diamagnetic quenchers are known to be strong electron acceptors, annihilate as a free-positron following a charge transfer mechanism (upper path), $\tau_F \simeq 0.45$ nsec in condensed matter. Two arguments can be made against the charge transfer mechanism. Although all quenchers are known to be strong electron acceptors, not all strong acceptors quench ortho-positronium, i.e. benzonitrile, benzaldehyde, and napthalene. Charge transfer is energetically possible in solution only if the following inequality is satisfied.

$$-I + A + Q + S > 0 \qquad (2)$$

where I is the ionization potential of the donor, A is the electron affinity of the acceptor, Q is the Coulomb interaction energy of the ions, and S is the solvation energy of the ions.[41] The ionization potential of positronium is constant and all compounds with large electron affinities should at least react to some extent with ortho-positronium. It is also difficult to envision the electron transfer step of the mechanism. The positronium atom does not have a nucleus in the usual chemical sense. Its positron and electron are light particles and should be delocalized in the PsM complex. Charge transfer in a complex of this nature has no significance in terms of molecular orbital theory. This does not exclude electron-transfer reactions of positronium via some other mechanism and indeed this has been observed.[42]

The second order rate constant for the reaction of ortho-positronium with M in Eq. (1) can be obtained as follows:[49]

$$-d[Ps]/dt = k[Ps][M] \tag{3}$$

Dividing by [Ps] yields

$$-d\ln[Ps]/dt = k[M] \tag{4}$$

Since $M \simeq M_o \gg Ps_o$, the reaction will appear to be pseudo-first-order. The left-hand-side of Eq. (4) is defined to be the rate of disappearance of positronium, λ_M. Therefore,

$$\lambda_M = k[M] \tag{5}$$

The ortho-positronium annihilation rate in a pure liquid such as benzene is $\lambda_2 (= \lambda_{Benzene})$ and

$$k_{Benzene} = \lambda_2/[Benzene] \tag{6}$$

The annihilation rate in benzene was measured to be 0.33 $nsec^{-1}$, this corresponds to a rate constant for the reaction of $2.96 \times 10^7 \ M^{-1}sec^{-1}$.

The annihilation rate for a solution is actually the sum of two rates, λ_S, the rate in the solvent, and λ_M, the rate due to the solute, M. If the solute is present in small concentration, i.e. millimolar, the following approximations are valid:[43]

$$\begin{aligned}[\text{Solvent}] &\approx \text{constant} \\ \lambda_S &\approx \text{constant}\end{aligned} \qquad (7)$$

and

$$\lambda_2 = \lambda_S + k_M[M] \qquad (8)$$

Any rate increase, $\lambda_2 - \lambda_S$ is due entirely to the solute. A plot of λ_2 versus [M] has a slope that is equal to the rate constant for the reaction between the ortho-positronium and M. An example of one such plot is given in Fig. 17 for nitrobenzene in benzene. The rate constant was found to be 27±2 M^{-1} $nsec^{-1}$, almost three orders of magnitude higher than rate constant for the reaction with benzene.

The general statements made in this section apply to all rapid reactions. For reasons of availability and numerous possible substituents, the nitroaromatics were chosen to be examined in this study. The following sections will deal with the ortho-positronium reaction with them.

B. Conjugation Effects

Conjugation, or lack of it as the case may be, is a major factor in determining the ability of a molecule to chemically quench ortho-positronium. The microwave spectrum of nitrobenzene shows that the molecule is planar[44] with an internal barrier to rotation of 1000 ± 500 cm^{-1}. When then the nitro group is co-planar with the aromatic ring, it has

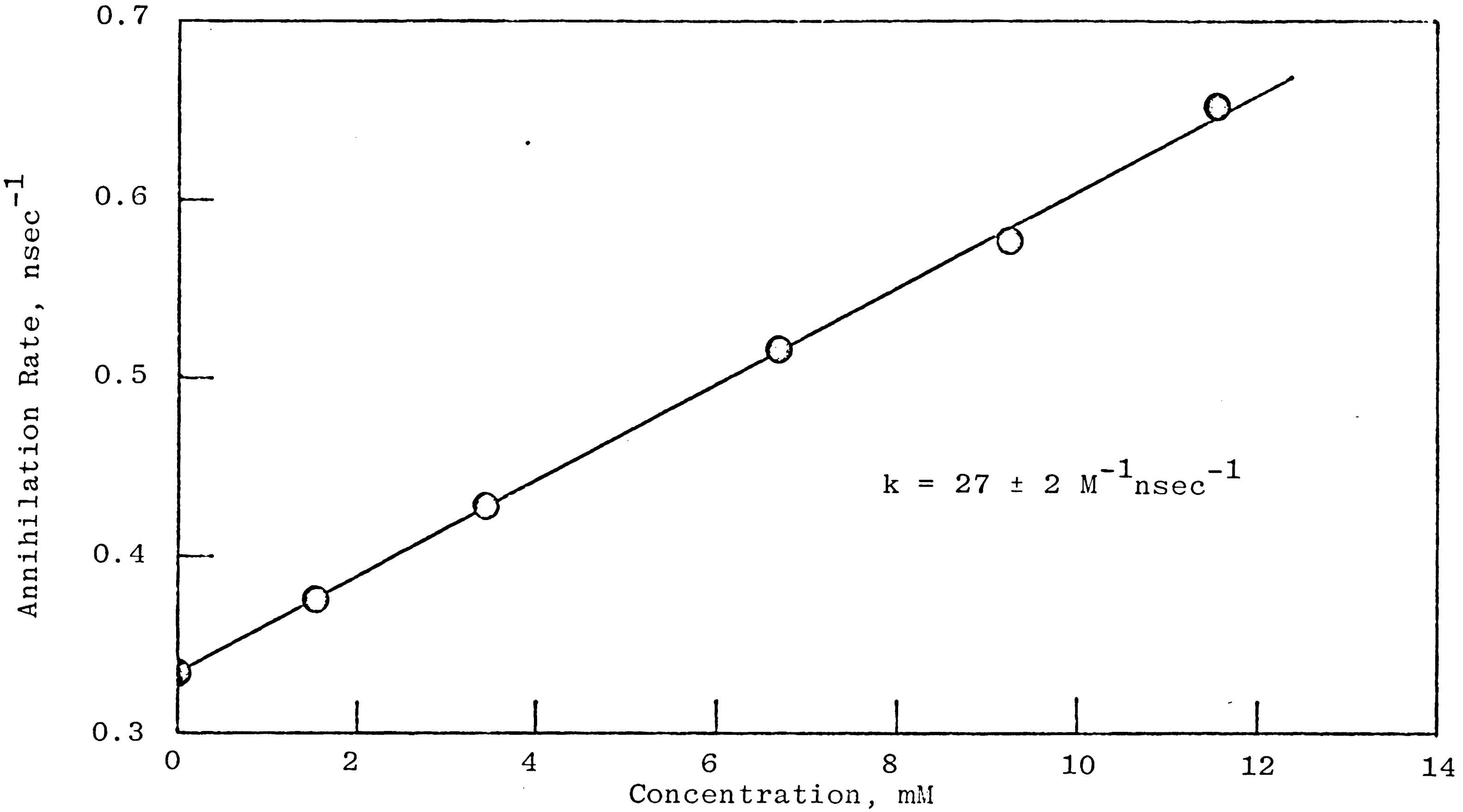
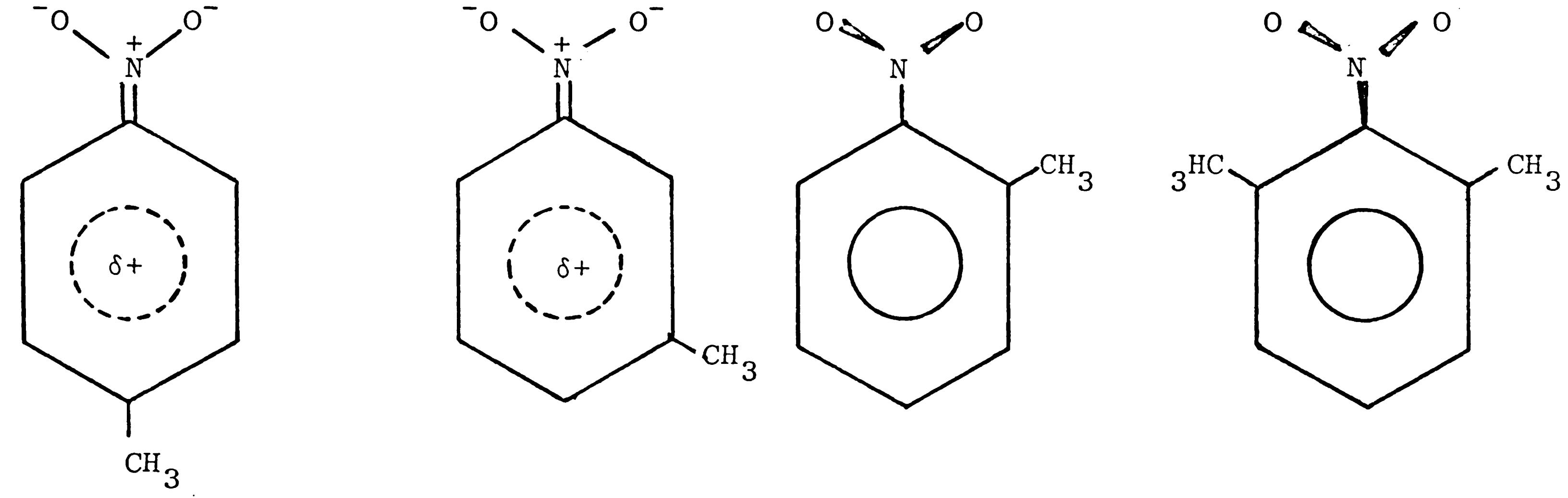


Figure 17. λ_2 versus Nitrobenzene Concentration in Benzene.

its maximum electron withdrawing effect and is best able to remove electron density from the ring.[45]

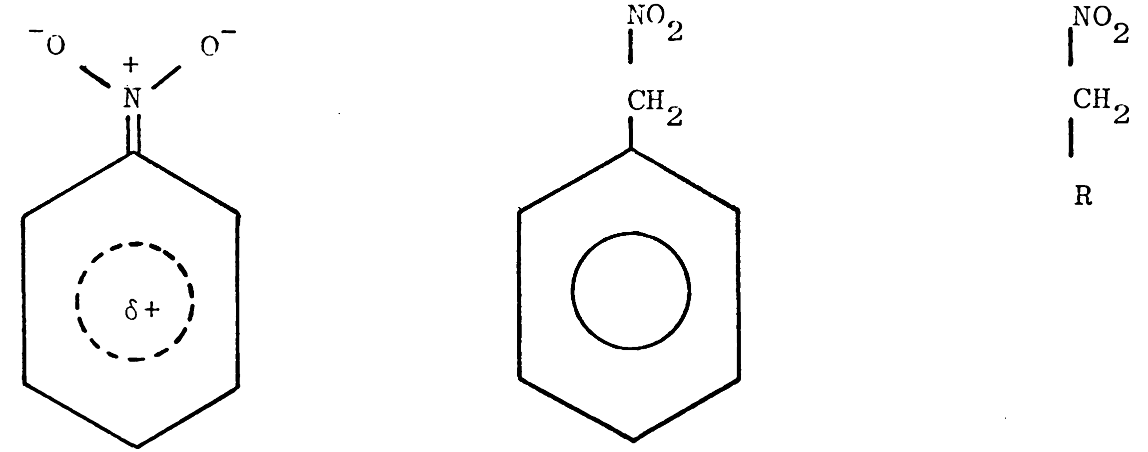
The steric interaction between the nitro group and the methyl group(s) in the ortho positron was used to measure the effect that conjugation losses had on the values of the measured rate constants. Methyl groups were convenient because their inductive and mesomeric effects are small. Toluene, like benzene, reacts very slowly with positronium, $k_{Tol.} \simeq 10^7\ M^{-1}sec^{-1}$. The observed rate constants for some model compounds are given in Fig. 18. Para- and meta-nitrotoluene react slightly slower than nitrobenzene itself, but the conjugation losses in the ortho isomer cause it to react only one-third as fast. If a second methyl group is placed adjacent to the nitro group, i.e. 2,6-dimethylnitrobenzene, the nitro group is twisted to an even greater extent out of the plane of the ring. It is therefore less able to conjugate with the ring and its corresponding rate constant drops further. This behavior was observed every time a large group was placed next to the nitro group (Appendix I lists all of the rate data taken in benzene solution at $295^{o}K$).

Isolating the nitro group from the π system was also found to have a drastic effect on the measured rate constants. In Figure 19, the rate constant for α-nitrotoluene is compared to that of nitrobenzene and found to be drastically



k = 22 $M^{-1}nsec^{-1}$ k = 21 $M^{-1}nsec^{-1}$ k = 8.5 $M^{-1}nsec^{-1}$ k = 0.39 $M^{-1}nsec^{-1}$

Figure 18. Steric Interactions that Force the Nitro Group out of the Plane of the Ring Cause a Reduction in the Rate Constant.



$k = 27\ M^{-1}nsec^{-1}$

$k = 0.15\ M^{-1}nsec^{-1}$

R:	$10^{-7}k$, $M^{-1}sec^{-1}$
-H	3.47
$-CH_3$	4.55
$-CH_2CH_3$	5.17

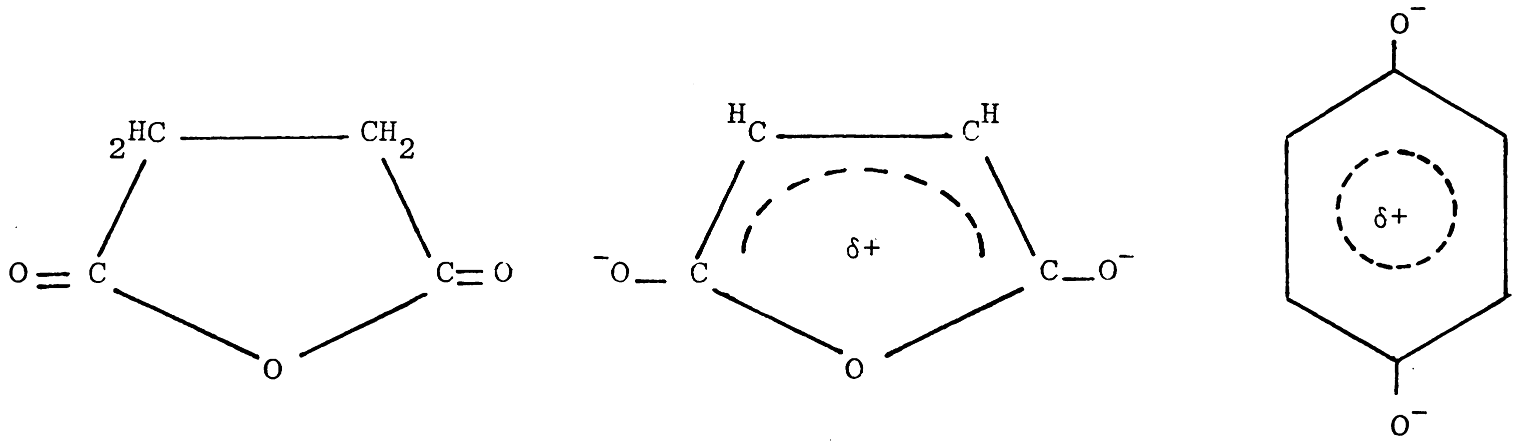
Figure 19. Nitro Compounds in Which the Nitro Group is Not Attached to a Conjugated System React Slowly with Ortho-Positronium.

reduced. Similar small reaction rate constants are observed for the nitroalkanes where there is no conjugation between the nitro group and the alkyl group.

A third way of examining the effect of conjugation is by measuring the rate constant for the reaction with certain anhydrides that contain varying amounts of conjugation. Fig. 20 shows a comparison of the observed positronium rate constants for the reaction with succinic and maleic anhydride. Succinic anhydride is unconjugated and exhibits a rate constant indicative of pickoff quenching. Conversely, maleic anhydride is highly conjugated and has resonance structures that place a delocalized positive charge on all four carbon atoms. The addition of the double bond caused the positronium rate constant to increase by a factor greater than 200, compared to succinic anhydride. These two are compared to the highly conjugated chemical quencher, parabenzoquinone which shows a much higher reaction rate constant.

C. Temperature Effects

If the mechanism given in Eq. (1) is correct, a study of the temperature dependence of the rate constants should provide information about the activation energy required to form the various PsM complexes. The solvent was changed from benzene to toluene for these experiments because it could be used over a much wider temperature range (200-500^{o}K).



k = 0.03 $M^{-1}nsec^{-1}$

k = 7.1 $M^{-1}nsec^{-1}$

k = 50 $M^{-1}nsec^{-1}$

Figure 20. Effect of Conjugation on Positronium Rate Constants.

First the temperature dependence of the solvent annihilation rate had to be determined in order to use Eq. (8) for calculating the rate constants. Fig. 21 shows a plot of λ_2 ($=\lambda_S$) versus T(^oC) for toluene. A linear least squares program was used to find the best fit to the data. It was found that

$$\lambda_S(T) = 0.3368 - (6.60 \times 10^{-4})\ T\ \text{nsec}^{-1} \qquad (9)$$

The second-order rate constant for toluene changed regularly from $3.45 \times 10^7\ M^{-1}sec^{-1}$ at -75^oC to $2.97 \times 10^7\ M^{-1}sec^{-1}$ at 170^oC.

When the annihilation rate of a 9.77 mM solution of nitrobenzene in toluene was measured over this temperature range, a rather interesting behavior was observed. The observed rate constant, k_{obs}, when plotted against the reciprocal Kelvin temperature, increased linearly from -75^oC up to approximately room temperature, $10^3/T^oK = 3.4$, and then decreased linearly as the temperature was raised further.[46] This is shown in Fig. 22. A comparison is made in this figure between the temperature dependence of the rate constants in toluene and the nitrobenzene solution. The difference between the two rate constants is greatest around room temperature. But at the high and low temperature ends they begin to approach each other. Deviations from typical Arrhenius behavior was found for other nitroaromatics. Fig. 23 shows the log k versus 1/T curves for p-

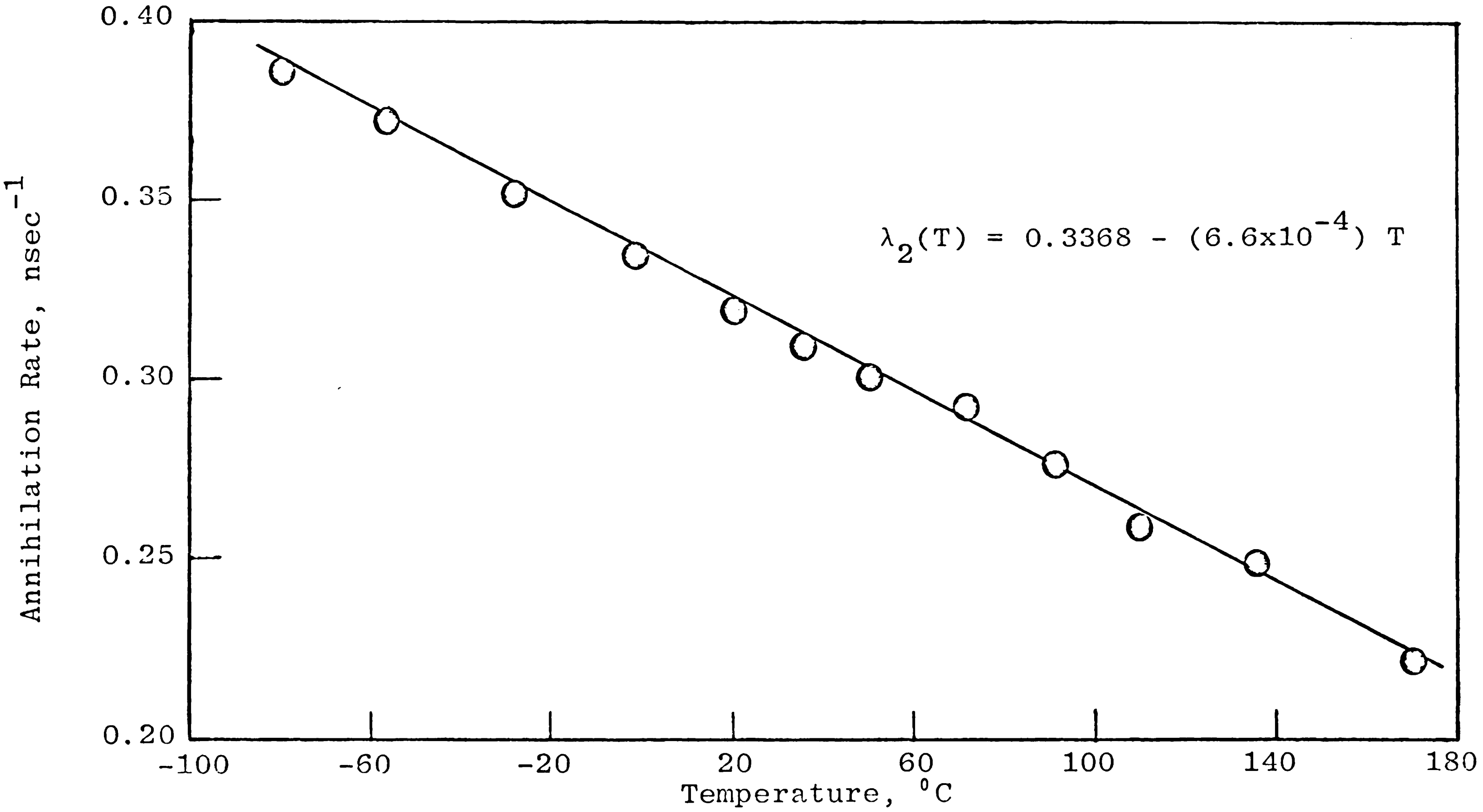


Figure 21. λ_2 versus T (°C) in Toluene.

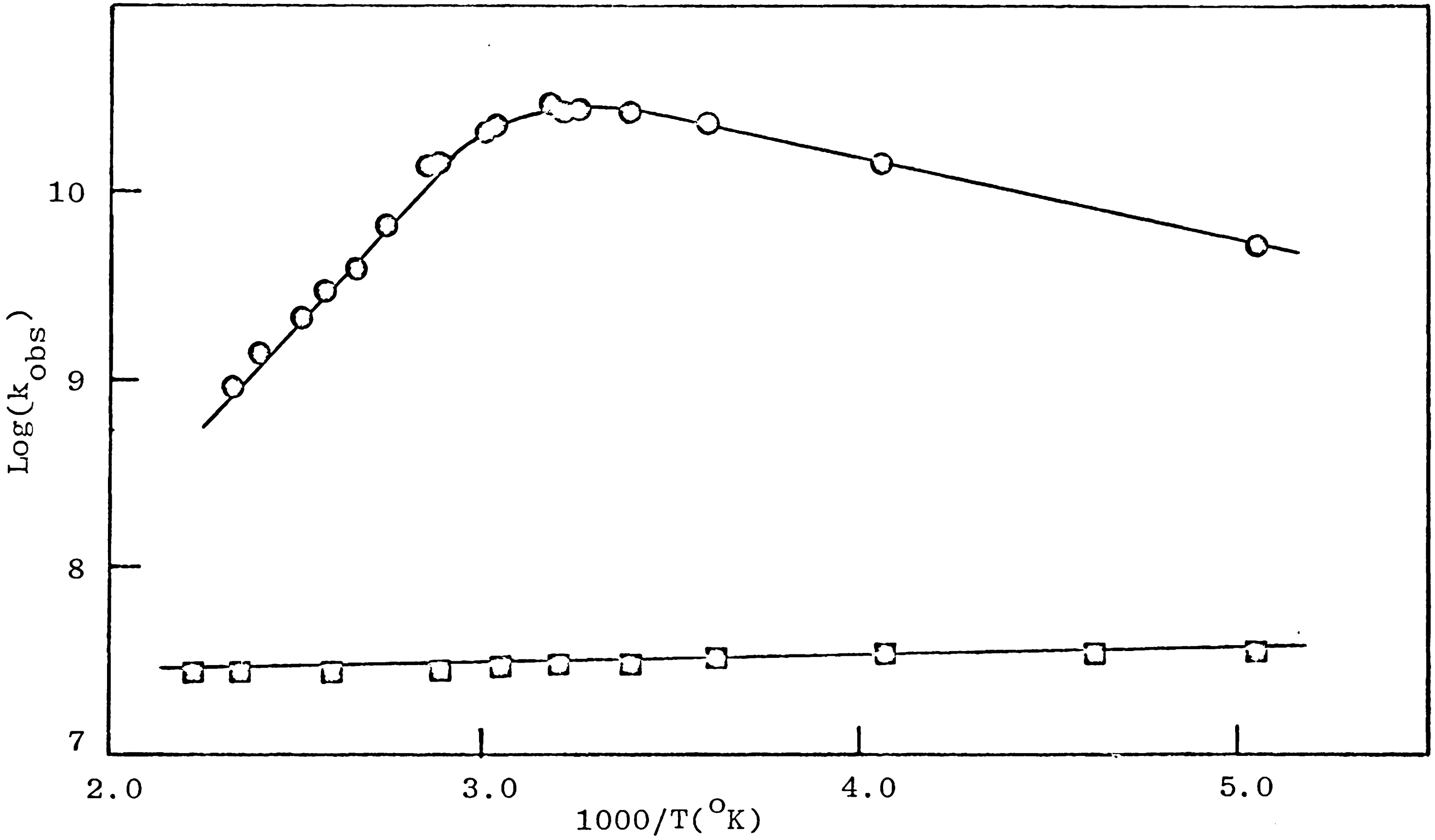


Figure 22. Arrhenius Plots for the Reaction of Ortho-Positronium With 9.77 mM Nitrobenzene in Toluene (○) and Pure Toluene (□).

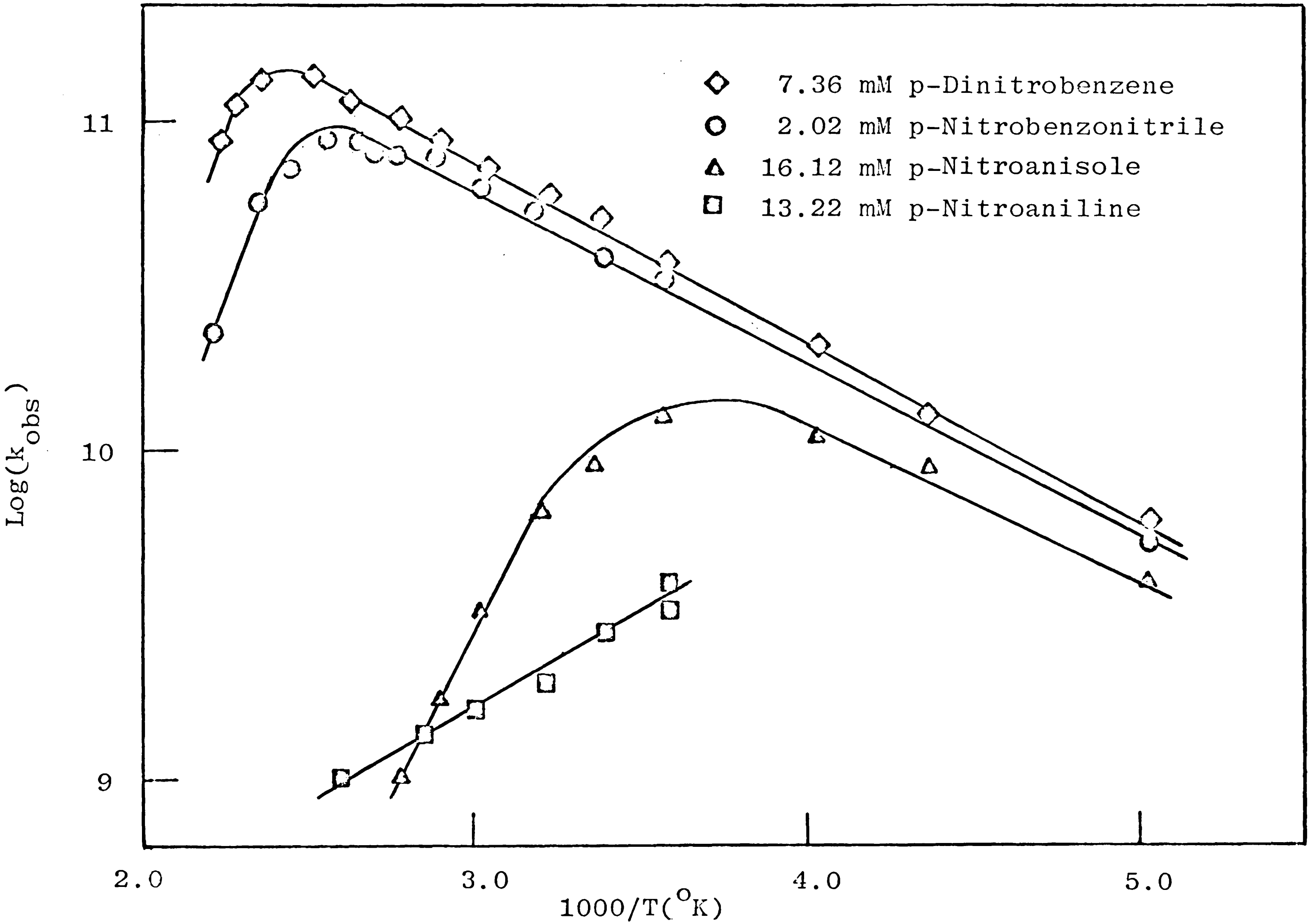


Figure 23. Arrhenius Plots for the Reaction of Ortho-Positronium with Various Nitroaromatics in Toluene.

dinitrobenzene, p-benzonitrile, p-nitroanisole, and p-nitroaniline. The Arrhenius portions of these five curves (this refers to the section of the curve with negative slope) all have approximately the same slope, while the non-Arrhenius sections (positive slope) have different slopes. p-Nitroaniline could not be run below 4°C due to its insufficient solubility in toluene below this temperature.

There are a variety of reactions that can cause deviation from the Arrhenius law. In principle, even the simplest kinetic processes should show a temperature dependence of the activation energy,[47] although it is rarely observed due to limited experimental temperature ranges or accuracy. Deviation from the Arrhenius law of a different nature can be found for reactions involving, for example equilibria, parallel, or consecutive processes.[48] This may be caused by a changing reaction pathway, rate determining step, or any process that causes the observed activation energy to change with temperature. For the type of deviation shown in Figures 22 and 23, where the measured activation energy actually becomes negative at high temperatures, only a few of these reactions are possible.

The inversion in the log k versus 1/T plot eliminates the possibility of a reaction involving a consecutive or parallel pathway. Deviation in the Arrhenius plot could occur by this method but both activation energies would be positive.

Formation of an unreactive substance in the sample might explain the observed behavior. The nitroaromatics could possibly decompose at higher temperature giving rise to a product that reacts more slowly. This possibility was ruled out experimentally. The data was obtained by first measuring the rate constant at room temperature followed by kinetic runs at increasingly higher temperatures. After the measurement was taken at the highest temperature, the sample was rerun at room temperature to check against decomposition. In all cases, the two room temperature values agreed within experimental error. Reversible formation of an unreactive species has not been ruled out by this procedure. For example, the positronium could react with a solvent-solute complex. Although nitroaromatics do form these complexes in toluene, the results in other solvents discounted this explanation. See the section on solvent effects in this chapter.

The positronium atom is expected to tunnel readily due to its low reduced mass.[49] However, the tunnel effect, when observed, usually causes a log k versus 1/T plot to curve rather than invert as in the present case. A tunneling calculation has been made for both a positron and positronium atom incident on a potential barrier of varying height and geometry.[50] The results indicate that the probability of tunneling is very high. To apply these results to the present situation is impractical at the present time. The shape of the barrier and the nature of the tunneling particle are not known. Figure 24 is a plot of log of the transmission coefficient versus particle energy for a positronium atom tunneling through a parabolic, square wave, and Eckart barrier, 1 Å wide and 20 kcal/mole high.[49] The initial results are encouraging and further work seems warranted.

A mechanism that satisfactorily explains the observed behavior is the following:

$$\mathrm{Ps} + \mathrm{M} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{PsM} \xrightarrow{k_2} \mathrm{M} + 2\gamma \qquad (10)$$

ortho-Positronium combines with the nitroaromatic molecule to form a PsM complex in a reversible step. This complex is thought to be of a nature in which the positron and electrons are completely delocalized. The electron and positron enter into different molecular orbitals of the complex. The complex can either go on to annihilate the positron, k_2, or decompose into an ortho-positronium atom and molecule, k_{-1}. Since the concentration of M remains essentially constant throughout the experiment, the mechanism can be simplified to

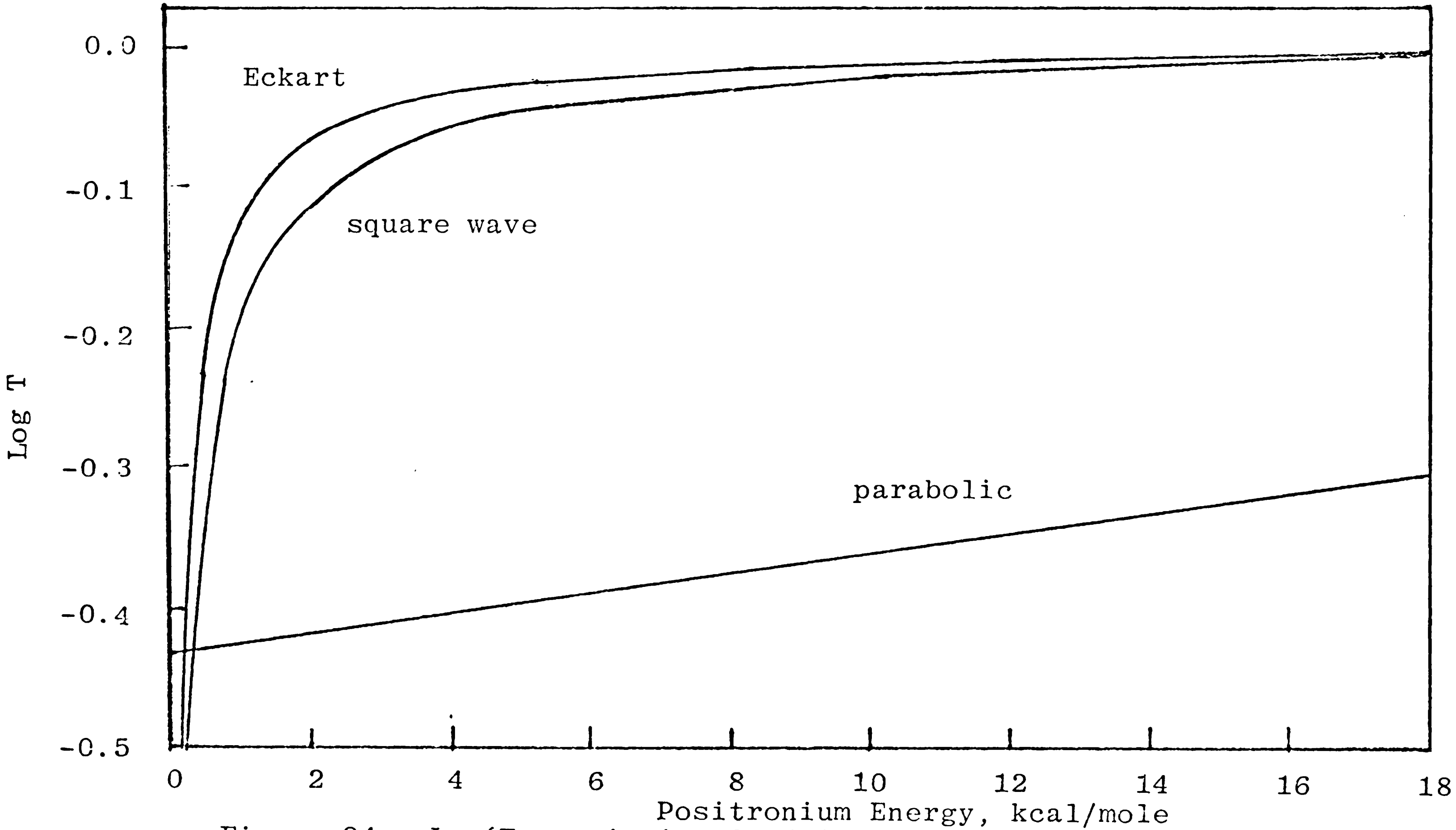


Figure 24. Log(Transmission Coefficient) versus Positronium Energy for Three Different Potential Barriers.

$$\mathrm{Ps} \underset{k_{-1}}{\overset{k_1'}{\rightleftharpoons}} \mathrm{PsM} \xrightarrow{k_2} \mathrm{M} + 2\gamma \qquad (11)$$

for $k_1' = k_1[M]$. For this mechanism, one obtains the following equations.

$$\begin{aligned} -d[\mathrm{Ps}]/dt &= k_1'[\mathrm{Ps}] - k_{-1}[\mathrm{PsM}] \\ d[\mathrm{PsM}]/dt &= k_1'[\mathrm{Ps}] - (k_{-1}+k_2)[\mathrm{PsM}] \\ d[2\gamma]/dt &= k_2[\mathrm{PsM}] \end{aligned} \qquad (12)$$

These differential equations can be solved exactly[51,52] for the time dependence of the concentration of Ps, PsM and M (or 2γ). The exact solutions are found to be functions of three parameters, S_1, S_2 and S_3.

$$\begin{aligned} S_1 &= (p-q)/2 \\ S_2 &= (p+q)/2 \\ S_3 &= 0 \end{aligned} \qquad (13)$$

where $p = k_1' + k_1 + k_2$ and $q = (p^2-4k_1'k_2)^{1/2}$. S_3 is related to the total equilibrium solution, the time independent terms. If $S_1 << S_2$, there is a simple time dependence of [Ps], [PsM] and [M] which involves only $\exp(-S_1t)$ after a short induction period. This inequality can be met if k_{-1}, $k_2 >> k_1'$ which is equivalent to invoking the steady-state assumption for the PsM complex. Letting $d[\mathrm{PsM}]/dt = 0$,

$$S_1 \simeq k_1{'}k_2/(k_{-1}+k_2) \simeq [k_1k_2/(k_{-1}+k_2)][M]$$

and

$$S_2 \simeq k_1+k_2 \qquad (14)$$

Therefore, if the steady-state assumption is valid, the observed rate constant for the disappearance of positronium (or the formation of 2γ) is $k_1k_2/(k_{-1}+k_2)$. In relation to Figures 22 and 23, the low temperature limiting line corresponds to a situation in which $k_2 >> k_{-1}$ so that the reaction rate, r, becomes

$$r = k_1[M][Ps] \qquad (15)$$

The high temperature limit corresponds to the situation in which $k_{-1} >> k_2$ and the reaction rate changes to

$$r = k_{EQ}k_2[M][Ps] \qquad (16)$$

where $k_{EQ} = k_1/k_{-1}$. The correct mechanism must predict that both the low and high temperature rate expressions be first order in M since this is observed experimentally.

The activation parameter obtained from the low temperature line represents the activation energy, $E_a(1)$, of the associative step, k_1. The high temperature line can be

$$k_1 = A_1 \exp(-E_a(1)/RT) \qquad (17)$$

used to measure the sum of two activation parameters, ΔH_{EQ} for the equilibrium step and the activation energy, $E_a(2)$ for the annihilation step.

$$k_2k_{EQ} = A_2A_1/A_{-1} \exp -\Delta H_{EQ}-E_a(2)/RT \qquad (18)$$

These are shown schematically in Figures 25 and 26.

A non-Arrhenius section is present in all the plots. The activation energy, $E_a(2)$, is always positive, therefore the results indicate that the PsM complex is more stable than the separated moieties. Chapter 4 deals primarily with this topic. Representing the barrier to annihilation as a thermodynamic barrier, as was done in Fig. 26, presented a problem that was never fully clarified.

The activation parameters for the reactions of the five nitroaromatics with positronium are listed in Table II. (The activation parameters for all reactions appear in Section E of Appendix I).

Two points can be made concerning the data taken in toluene. The activation energies for the first step were all small, approximately 1.0 kcal/mole, and fairly constant throughout. This is indicative of a fast reaction. It is interesting to note that if the second substituent on the nitrobenzene molecule was electron withdrawing, the ΔS_a (-26^oC) was more unfavorable. The order being $OCH_3 >$ H $>$CN NO_2. The change in entropy was calculated from the average value of the activation energy, $E_a(1)$, in toluene by using the following equation:

$$k_1 = \kappa kT/h \exp(\Delta S_a/R) \exp(-E_a(1)/RT) \qquad (19)$$

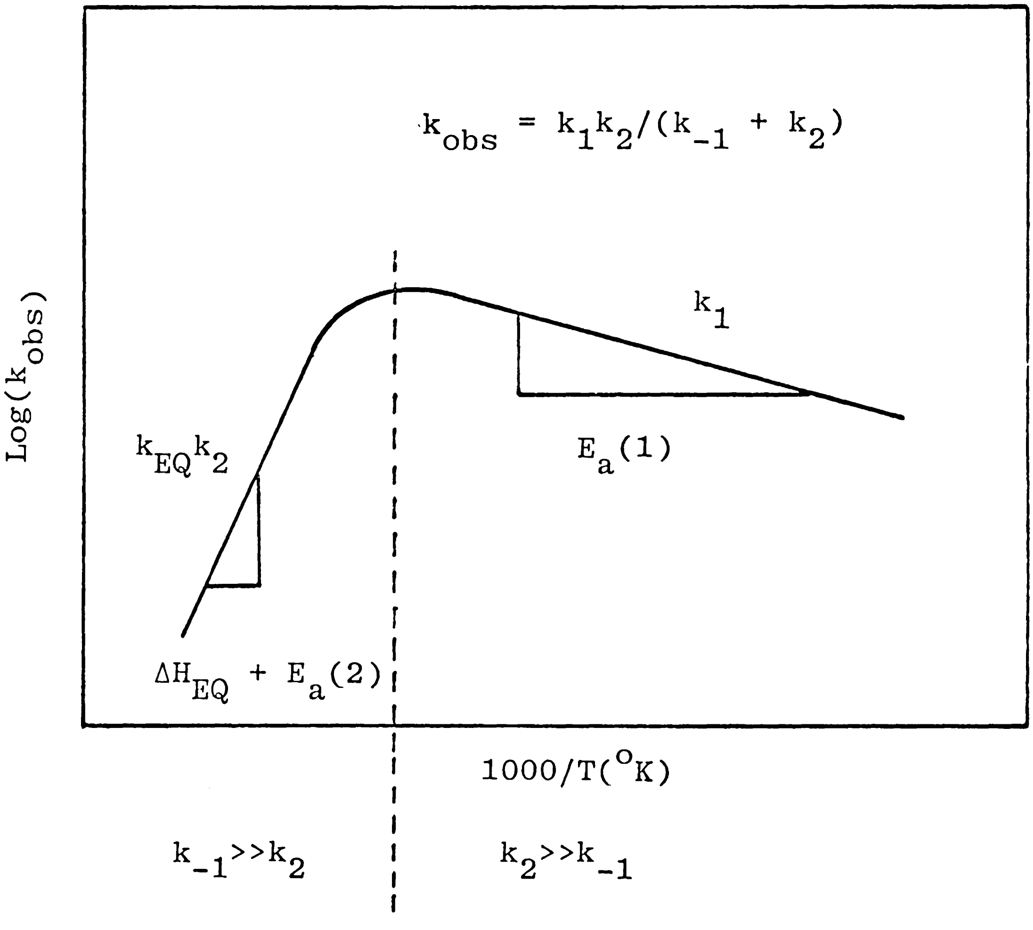


Figure 25. Typical Arrhenius Plot for the Reaction of Ortho-Positronium with Nitroaromatics Showing the Thermodynamic Parameters.

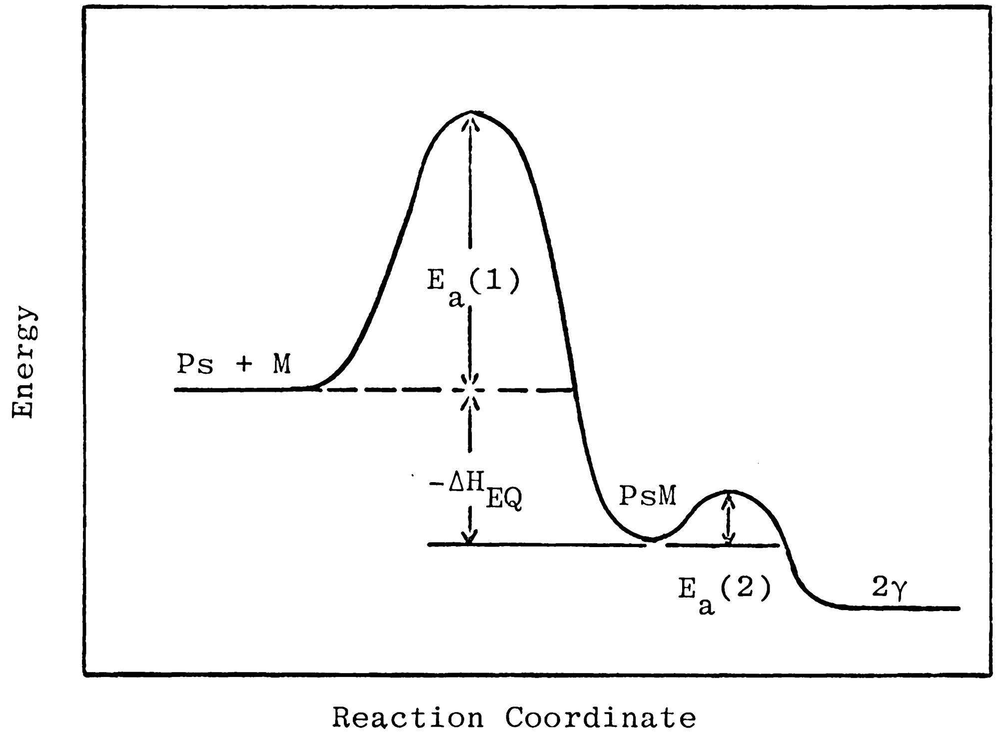


Figure 26. Potential Energy Surface for Ortho-Positronium Reacting with a Nitroaromatic Molecule.

Table II. Thermodynamic Data for the Reactions of o-Ps in Toluene

	Low Temperature Limit		High Temperature Limit
Compound	$E_a(1)$, kcal/mole	$\Delta S_a(-26^{\circ}C)$, eu*	$\Delta H_{EQ} + E_a(2)$, kcal/mole
p-Nitroaniline	---	---	-1.1 ± 0.1
2,6-Dimethylnitrobenzene	---	---	-2.7 ± 0.3
p-Nitroanisole	0.9 ± 0.1	-10.2	-3.6 ± 0.3
Nitrobenzene	0.8 ± 0.1	-9.7	-4.5 ± 0.3
p-Nitrobenzonitrile	1.0 ± 0.1	-9.2	-6.0 ± 0.5
p-Dinitrobenzene	1.1 ± 0.1	-8.9	<-4.0
p-Benzoquinone	1.0 ± 0.1	-10.5	-7.5 ± 0.5

* Calculated using the average E_a (1) value.

The concept of entropy changes as applied to positronium complexes has not been reported previously. In terms of reorganizing the positronium atom and molecule into a complex, the results would tend to indicate that the complex would more readily proceed to the transition state with molecules containing electron deficient substituents.

A qualitative analysis of the stability of the complexes can be obtained from the high temperature region of the graphs. $\Delta H_{EQ} + E_a(2)$ is always negative. This indicates that $E_a(2)$ is relatively small because even when complex formation is least likely, ΔH_{EQ} is negative but small, the sum of the two energies is still negative.

The ability of nitrobenzene to complex with positronium is probably the reason that it is the only mono-substituted benzene known to rapidly react with ortho-positronium. In order to react, the main requirements appear to be: (1) conjugation, (2) strong electron withdrawing substituents, and (3) an ability of the molecule to form strong molecular complexes.[53] It has been shown[41], that compounds that form very strong molecular complexes, such as 7,7,8,8-tetracyanoquinodimethane (TCNQ) and tetracyanoethylene (TCNE), react at least an order of magnitude faster than nitrobenzene, which forms rather weak complexes.

It was initially thought that the inversion in the log k versus 1/T plots was caused by a conjugation effect as described in the previous section. As the temperature was increased, the nitro group would begin to rotate out of the plane of the ring, and the observed rate constant would decrease due to a loss of conjugation. For this reason, the annihilation rate for a p-benzoquinone was measured as a function of temperature. The Arrhenius plot is given in Figure 27. p-Benzoquinone is known to react faster than nitrobenzene with positronium and it also readily forms molecular complexes. If the inversion was caused by a loss of conjugation, the effect should not be seen for p-benzoquinone which does not have a functional group that could rotate out of the plane of the ring. However, it behaved in a similar manner to the nitroaromatics, $E_a(1) = 1.0$ kcal/mole and $\Delta H_{EQ} + E_a(2) = -7.5$ kcal/mole, and the mechanism given in Eq. 10 was retained.

The log k_{obs} versus 1/T plot for 2,6-dimethylnitrobenzene is also shown in Figure 27. This compound showed unusual behavior in that no Arrhenius portion of this curve was found. Instead of inverting, the curve remains constant over a $50^{\circ}C$ range. Either the complex is so weakly bound due to the large loss of conjugation caused by the steric-interaction between the two methyl groups and the nitro group that it decomposes rapidly or lower temperature data are needed to see the break.

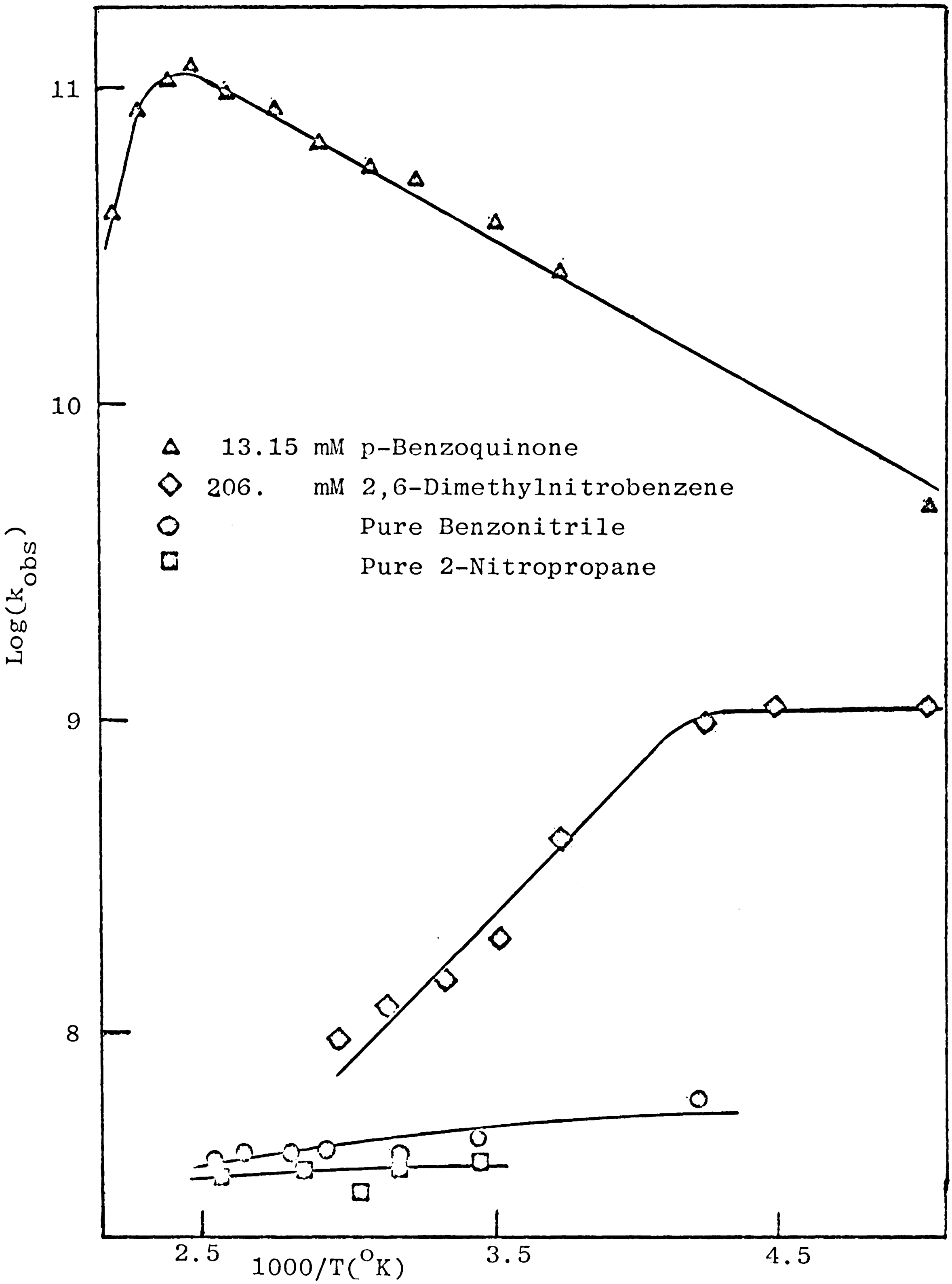


Figure 27. Arrhenius Plots for the Reaction of Ortho-Positronium with p-Benzoquinone, 2,6-Dimethylnitrobenzene, Benzonitrile and 2-Nitropropane in Toluene.

It was mentioned previously that benzonitrile and 2-nitropropane react very slowly with positronium at room temperature. Their complexes might not be stable at room temperature but data taken at other temperatures could possibly show compound formation. Figure 27 clearly shows no evidence for compound formation with these two compounds in the temperature range studied.

D. Solvent Effects

Similar Arrhenius data were taken using n-heptane and n-pentanol as the solvents. The temperature dependence of the solvent annihilation rate was measured and can be found in Section D of Appendix I. Only three nitroaromatic compounds were used to study the effect of the solvent on these reactions; nitrobenzene, p-nitroanisole, and p-dinitrobenzene. The Arrhenius plots and thermodynamic data appear in Figures 28 and 29 and in Table III respectively. Similar trends were found in these solvents. Figure 30 shows a comparison of the Arrhenius plots for the reaction of ortho-positronium with nitrobenzene in all three solvents. Since an inversion was seen in the Arrhenius plot obtained in n-heptane, the possibility of a solvent-solute species being responsible for the rapid reaction was now eliminated. Nitroaromatics are not known to form molecular complexes with alkanes.

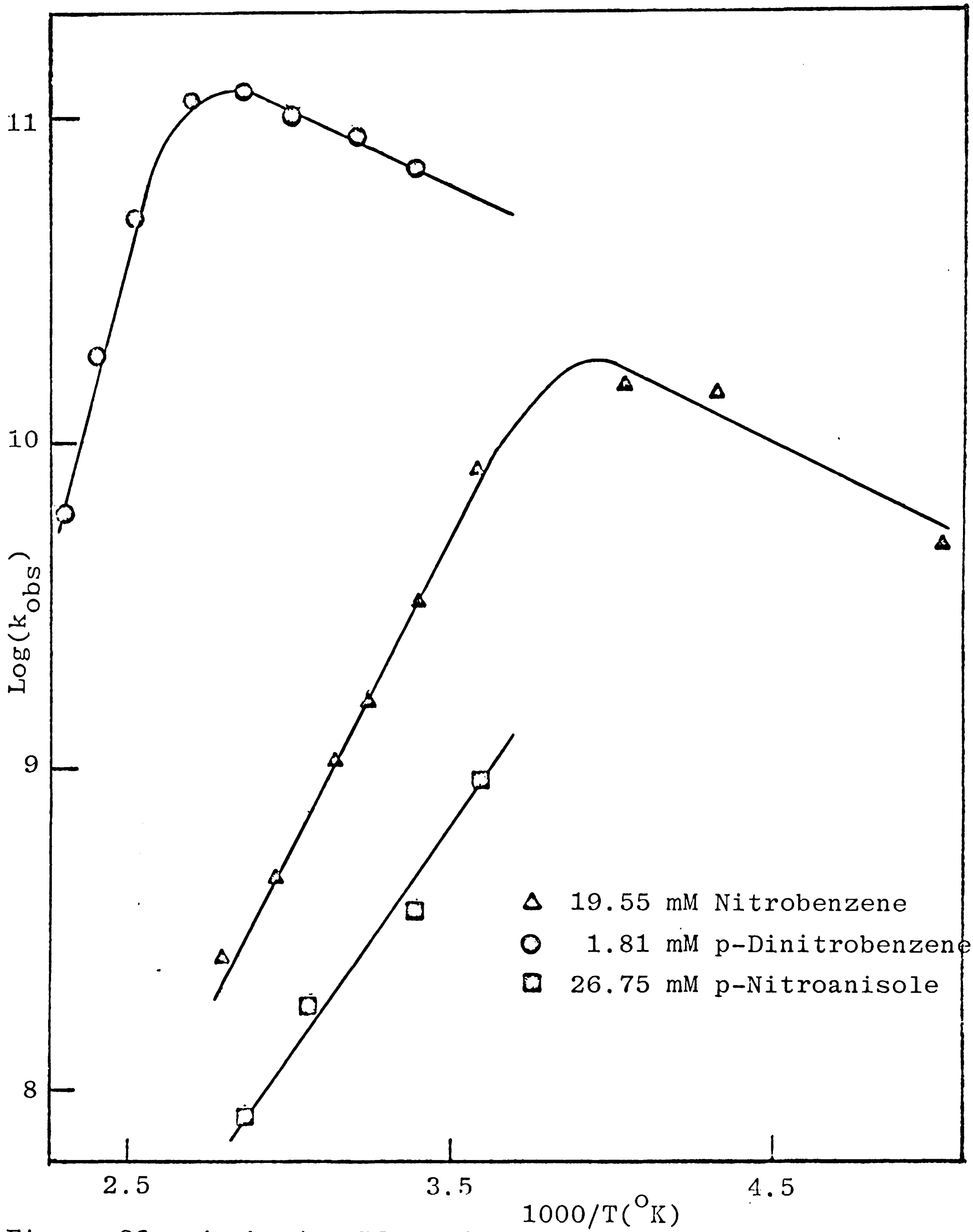


Figure 28. Arrhenius Plots for the Reaction of Ortho-Positronium with Nitrobenzene, p-Dinitrobenzene and p-Nitroanisole in n-Heptane.

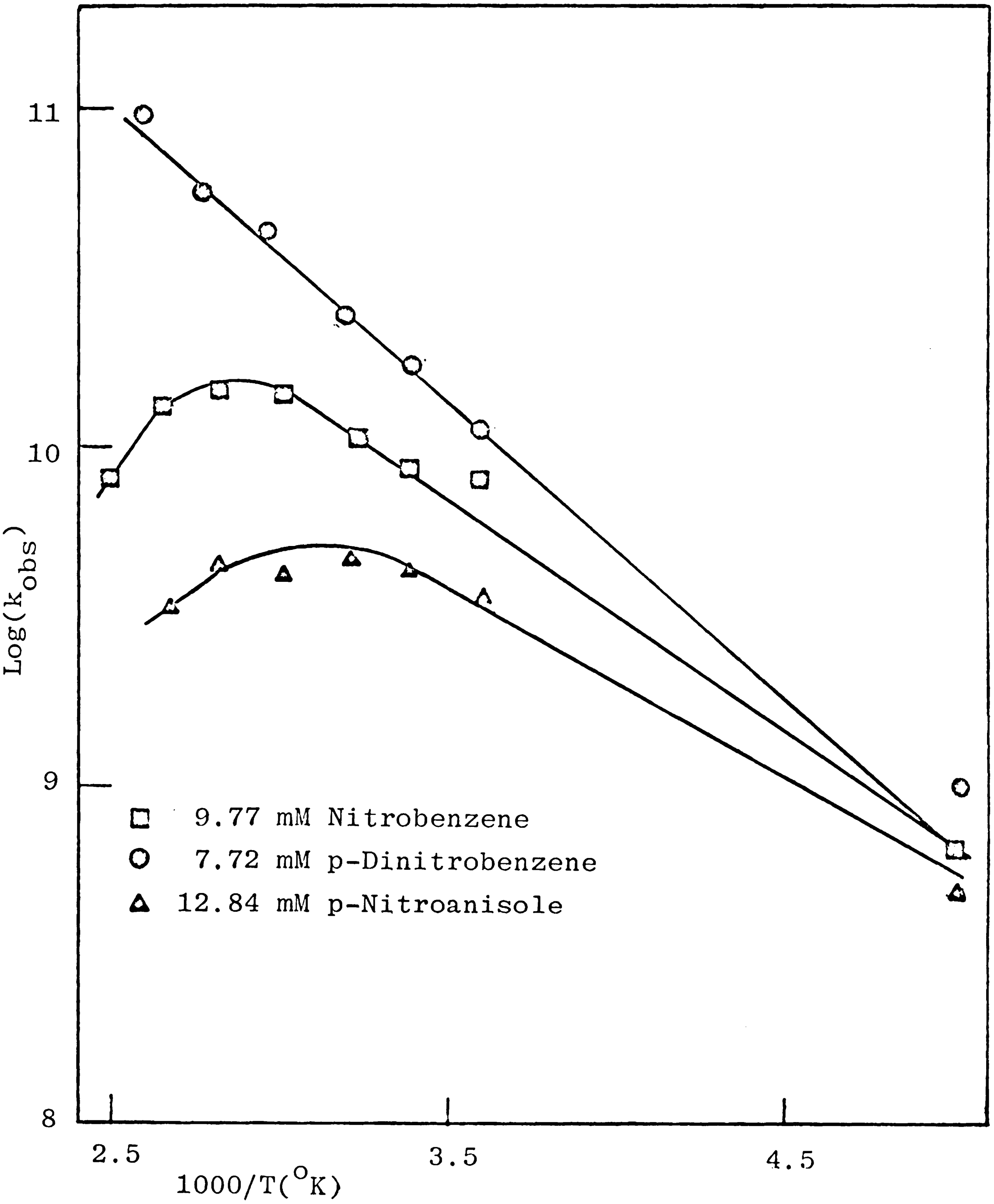


Figure 29. Arrhenius Plots for the Reaction of Ortho-Positronium with Nitrobenzene, p-Dinitrobenzene and p-Nitroanisole in n-Pentanol.

Table III. Thermodynamic Data for the Reactions of o-Ps in n-Heptane and n-Pentanol

	Low Temperature Limit		High Temperature Limit
Compound	$E_a(1)$, kcal/mole	$\Delta S_a(-26^{o}C)$, eu*	$\Delta H_{EQ} + E_a(2)$, kcal/mole
Solvent: n-Heptane			
p-Nitroanisole	---	---	-2.9 ± 0.4
Nitrobenzene	1.3 ± 0.2	-8.1	-4.4 ± 0.4
p-Dinitrobenzene	1.0 ± 0.2	-7.1	-8.0 ± 1.0
Solvent: n-Pentanol			
p-Nitroanisole	1.2 ± 0.1	-7.3	-1.3 ± 0.8
Nitrobenzene	1.3 ± 0.2	-6.2	-3.5 ± 0.6
p-Dinitrobenzene	1.8 ± 0.3	-5.5	---

* Calculated using the average $E_a(1)$ value.

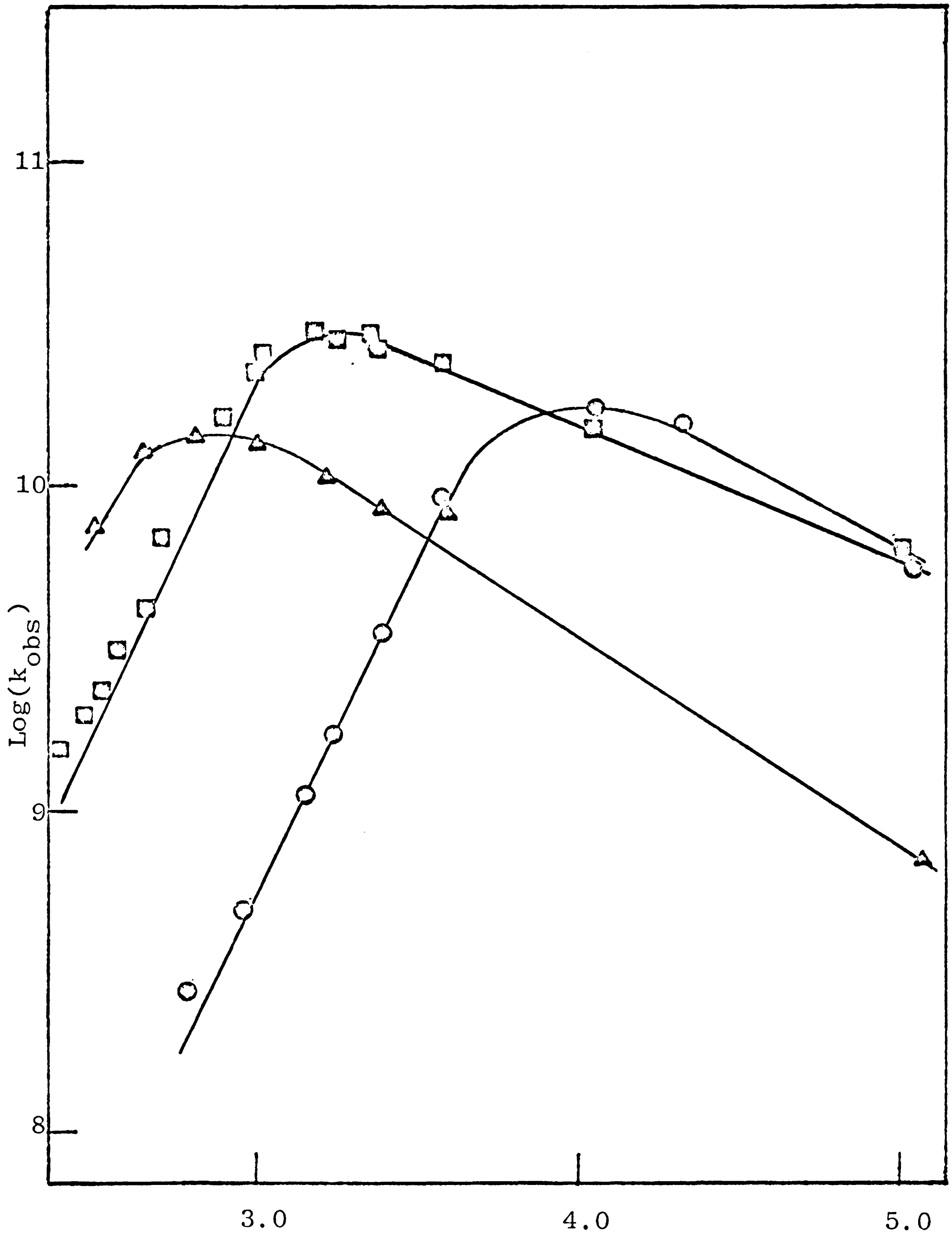


Figure 30. Arrhenius Plots for the Reaction of Ortho-Positronium with Nitrobenzene in (□) Toluene, (○) n-Heptane and (△) n-Pentanol.

The point of inversion in the curves is determined by the slopes of the two limiting lines and the pre-exponential factor, A, for each observed rate constant. These are A_1 for the low temperature limiting line and A_1A_2/A_{-1} for the high temperature limiting line. According to absolute rate theory, these factors contain two terms that could possibly affect the point of inversion. The first is the transmission coefficient, κ, and the second is the entropy change. The inversion point in the nitrobenzene curves of Figure 30 can be used to determine the ability of each solvent to assist in reaching the transition state before forming the PsM complex. For nitrobenzene and the other two compounds, this ability increased following the order

$$\text{n-pentanol} > \text{toluene} > \text{n-heptane} \qquad (20)$$

This is the order expected when neutral species combine to form charged or polar complexes.[53] The more polar the solvent, the more able it is to neutralize the charge separation.

E. Correlations

Many correlations were attempted before the temperature effect of Section C was discovered.[54-56] Numerous rate constants for substituted nitrobenzene compounds were measured in benzene at 295°K. The log of the relative rate constants (relative to nitrobenzene) was correlated to a variety of molecular parameters that included the energy of the lowest unoccupied molecular orbital (LUMO), the net π charge density of the aromatic ring, free valence, radical localization energy, etc. The results were moderately good considering that the observed rate constants were for different combinations of k_1, 1_{-1} and k_2.

The reactivity of these compounds toward positronium atoms at room temperature was correlated by use of the Hammett equation for electrophilic and nucleophilic attack.[57] Again, the observed rate constants could be k_1, $k_1k_2/(k_{-1}+k_2)$, or $k_{EQ}k_2$ depending on where the inversion point occured in the Arrhenius plot. An example of this can be found in Figure 23. At room temperature, the observed rate constant for p-nitroaniline is $k_{EQ}k_2$, for p-nitroanisole it is $k_1k_2/(k_{-1}+k_2)$, and for p-dinitrobenzene it is k_1. However, it was found that around -25°C, most measured rate constants are k_1. Figure 31 is a Hammett plot for nucleophilic attack[58] using only k_1 rate constants as measured in toluene at -25°C.[59] These preliminary results are encouraging and further work at this low temperature seems warranted.

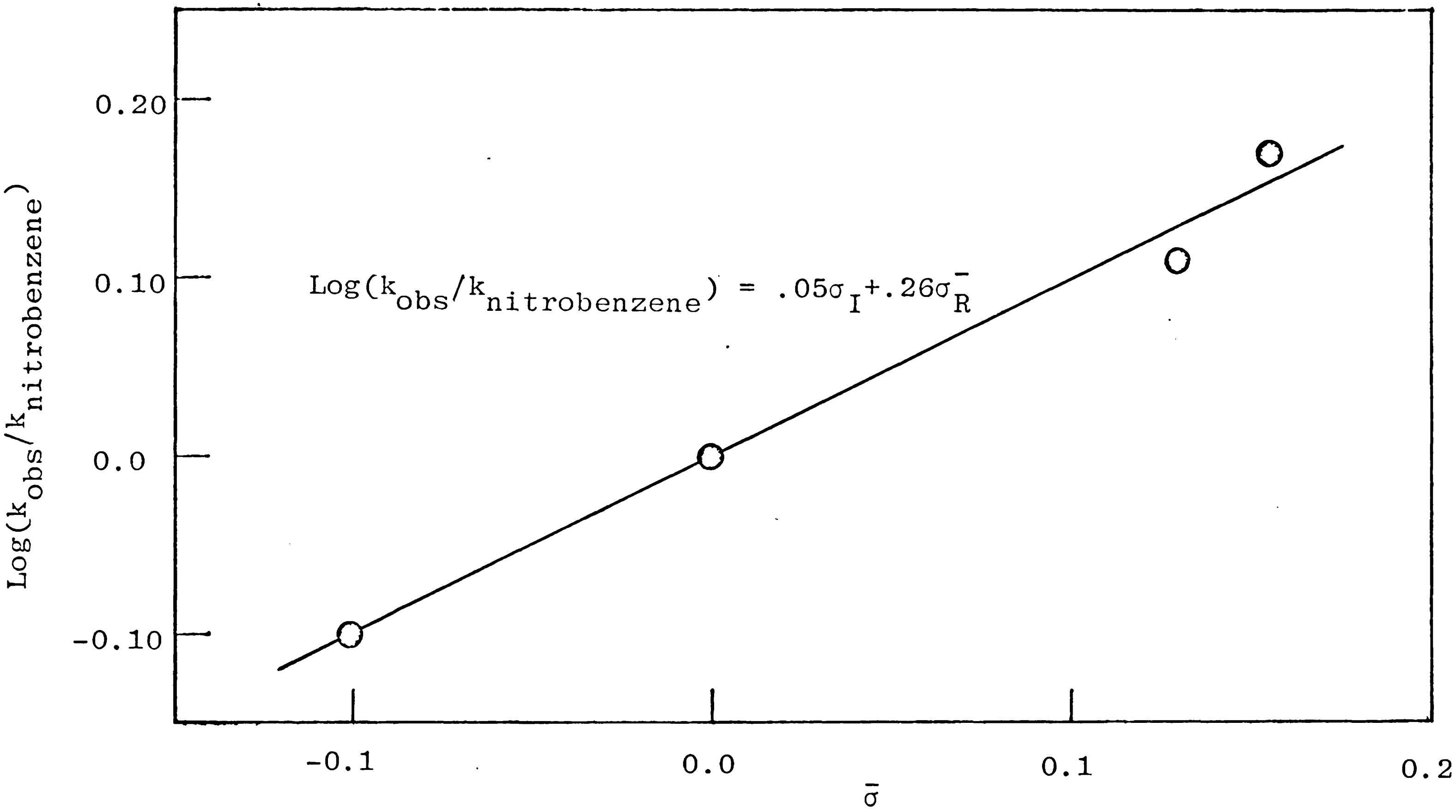


Figure 31. Hammett Plot for the Reaction of Ortho-Positronium with Substituted Nitraromatics in Toluene at -26°C.

POSITRON AND POSITRONIUM COMPLEXES[60]

A. Introduction

There is now a considerable amount of evidence available both from this work as well as lifetime and angular correlation experiments to indicate the existence of stable positron and positronium complexes with atoms, ions, and molecules.[8,26,61-65] Theoretical calculations of the stability of positron complexes with atoms and atomic ions, and of the positron lifetimes in these complexes have generally been rewarding.[61,66-69] The most extensive theoretical work in this area has been done by Schrader and co-workers: a 1970 paper[70] provides a general non-relativistic self-consistent-field theory of one-positron, many electron systems and explains the approximations involved in most of the earlier work; a more recent paper describes a variational treatment of e^+H^- which incorporates interparticle coordinates in the wavefunction.[69] The most accurate result of Navin, Schrader, and Lebeda[69] indicates that e^+H^- is 0.794 eV more stable than separated positronium and hydrogen atoms. This means that the positron binding energy (positron affinity) of the hydride ion is on the order of 6.8 eV. Earlier calculations indicated positron affinities on the order of 2 eV for Cl^- and alkali atoms.[61,67]

This chapter is concerned with the existence of positron complexes with relatively large organic compounds. For large compounds, containing many electrons, a variational treatment similar to that for e^+H^- is presently intractable, and it is necessary to retreat to some form of the self-consistent-field theory.[70] We take the natural approach of employing the Born-Oppenheimer separation and the Hartree-Fock approximation. The former implies that we treat the nuclei as fixed point charges, and the latter, that we treat the positron on an equal basis with the electrons, calculating only average Coulombic interactions between all light particles. In general this approach should give reasonable results. The necessary corrections for more accurate calculations will arise from short-range interparticle potentials, and should be amenable to treatment by an extension of Sinanoglu's theory of purely electronic correlation effects.[71] The positron-electron correlation effects are expected to be extremely important in the prediction of positron annihilation rates, so we have not tried to calculate these; we are concerned here only with the stability of the positron and positronium complexes.

We make use of the approximate all-valence-electron self-consistent-field theory developed by Pople and coworkers,[72] the so-called CNDO/2 approximation. We seek positronic and electronic molecular orbitals and express both as linear combinations of the same set of Slater-type atomic orbitals.[72,73] This has the advantage of providing a basis for estimating the necessary integrals over positron coordinates without a great deal of computation. For all electronic matrix elements, the CNDO/2 approximations and the parameterization suggested by Pople and Beveridge were retained. The positronic matrix elements of the core Hamiltonian were estimated by comparison with the corresponding electronic integrals. The latter were approximately decomposed into kinetic and potential energy parts using the virial theorem. A sign change of the potential part provided the approximation for the one-center positron matrix elements. For the two-center core matrix elements, these considerations were combined with the Wolfsberg-Helmholtz approximation[74] and the formulation given by Cusachs and Cusachs.[75] All Coulomb integrals were evaluated using the CNDO/2 approximations, but accounting of course for the positive charge of the positron. It is recognized that these procedures only provide first approximations. In particular, the virial theorem is not strictly applicable to the electronic integrals involving Slater-type orbitals, and the Slater-type orbitals provide improper cusp behavior for the positron wavefunctions.

The calculations in this chapter deal primarily with positron complexes with closed shell molecules. By making use also of the lowest unoccupied electronic molecular orbital, we obtain a first approximation for the binding energies of positron complexes with molecular anions.

(These are alternatively referred to as positronium-molecule complexes).

B. Hartree-Fock Theory

The total Hamiltonian, in atomic units, for a one-positron 2n-electron system is given by

$$H = \sum_{\mu} h_{\mu}^{\text{core}(-)} + \sum_{\mu<\nu} g_{\mu\nu} + h_{p}^{\text{core}(+)} + \sum_{\mu} g_{\mu p}, \qquad (1)$$

where (using atomic units)

$$h_{\mu}^{\text{core}(-)} = -\nabla_{\mu}^{2}/2 - \sum_{\alpha} Z_{\alpha}/r_{\mu\alpha}$$

$$h^{\text{core}(+)} = -\nabla_{p}^{2}/2 + \sum_{\alpha} Z_{\alpha}/r_{p\alpha}$$

$$g_{\mu\nu} = r_{\mu\nu}^{-1}$$

$$g_{\mu p} = -r_{\mu p}^{-1}$$

The subscripts μ and ν are used to indicate electron terms, p indicates positron terms, and α refers to nuclei. The superscripts (-) and (+) will be used with electron and positron terms respectively for clarity. The core Hamiltonian terms include the kinetic energies and Coulombic interactions with all nuclei of the molecule. For a system containing 2n electrons, and one positron, the wave function is

$$\psi = \psi_{p}(p)[(2n)!]^{-1/2} \det|\psi_{1}(1)\ \psi_{2}(2)\cdots\psi_{2n}(2n)|, \qquad (2)$$

where each function, ψ_i, is a product of a molecular orbital, ϕ_i, and a spin wavefunction, either α or β. The positron spin is arbitrary. Since we are dealing with a closed-shell electronic system, each occupied electronic orbital occurs twice, being associated once with spin function α and once with β. We make the usual assumptions of orthonormality:

$$<\phi_p|\phi_p> \;=\; 1;\; <\phi_i|\phi_j> \;=\; \delta_{ij} \;. \tag{3}$$

The energy expectation value is

$$\begin{aligned} E = <\psi|H|\psi> \;=\; & <\psi|\sum_{\mu}^{2n} h_{\mu}^{core(-)}|\psi> + <\psi|\sum_{\mu<\nu}^{2n} g_{\mu\nu}|\psi> \\ & + <\psi|h_p^{core(+)}|\psi> + <\psi|\sum_{\mu}^{2n} g_{\mu p}|\psi>. \end{aligned} \tag{4}$$

Using the fact that the electronic part of ψ consists of <u>n</u> doubly occupied orbitals, this can be written in terms of summations over those molecular orbitals,

$$\begin{aligned} E = 2\sum_{i}^{n} H_{ii}^{(-)} + 2\sum_{i<j}^{n} (2J_{ij}^{(-)} - K_{ij}^{(-)}) + H_{pp}^{(+)} \\ + 2\sum_{i}^{n} J_{pi}^{(+-)} \end{aligned} \tag{5}$$

Here, $H_{pp}^{(+)}$ and $J_{pi}^{(+-)}$ are respectively the positron-core and positron-electron contributions,

$$H_{pp}^{(+)} = <\phi_p|h_p^{core(+)}|\phi_p>, \tag{6}$$

$$J_{pi}^{(+-)} = - <\phi_p(p)\phi_i(i)|r_{ip}^{-1}|\phi_p(p)\phi_i(i)>, \qquad (7)$$

and $H_{ii}^{(-)}$, $J_{ij}^{(-)}$, and $K_{ij}^{(-)}$ are the purely electronic core interactions, Coulomb and exchange integrals involving the molecular orbitals indicated by the subscripts. The molecular orbitals are expanded as linear combinations of the atomic valence-shell orbitals $\{\chi_\mu\}$,

$$\phi_i = \sum_{\mu}^{m} \chi_\mu C_{\mu i} , \quad \phi_p = \sum_{\mu}^{m} \chi_\mu C_{\mu p} \quad . \qquad (8)$$

If we introduce charge-density and bond-order matrices for both electrons and the positron,

$$P_{\mu\nu}^{(-)} = 2 \sum_{i}^{n} C_{\mu i}^{*} C_{\nu i} , \quad P_{\mu\nu}^{(+)} = C_{\mu p}^{*} C_{\nu p} , \qquad (9)$$

the energy can be written in terms of integrals over atomic orbitals:

$$\begin{aligned} E = & \sum_{\mu,\nu}^{m} P_{\mu\nu}^{(-)} H_{\mu\nu}^{(-)} \\ & + (1/2) \sum_{\mu,\nu,\lambda,\sigma}^{m} P_{\mu\nu}^{(-)} P_{\lambda\sigma}^{(-)} [<\chi_\mu(1)\chi_\lambda(2)|r_{12}^{-1}|\chi_\nu(1)\chi_\sigma(2)> \\ & - (1/2)<\chi_\mu(1)\chi_\lambda(2)|r_{12}^{-1}|\chi_\sigma(1)\chi_\nu(2)>] + \sum_{\mu,\nu}^{m} P_{\mu\nu}^{(+)} H_{\mu\nu}^{(+)} \\ & - \sum_{\mu,\nu,\lambda,\sigma}^{m} P_{\nu\sigma}^{(-)} P_{\mu\lambda}^{(+)} <\chi_\mu(p)\chi_\nu(1)|r_{1p}^{-1}|\chi_\lambda(p)\chi_\sigma(1)> \quad . \end{aligned} \qquad (10)$$

Again, the first two terms are identical with those arising in the simple closed shell electronic case,[72] and the latter two are caused by the positron,

$$H^{(+)}_{\mu\nu} = \langle\chi_\mu(p)|\, h_p^{\mathrm{core}(+)} |\chi_\nu(p)\rangle \tag{11}$$

Minimizing the energy with respect to variations in the electronic and positronic orbitals leads to two sets of Hartree-Fock equations,

$$\begin{aligned} F^{(-)}\,\phi_i &= \varepsilon_i\,\phi_i \\ F^{(+)}\,\phi_p &= \varepsilon_p\,\phi_p \quad , \end{aligned} \tag{12}$$

where the electron and positron Fock operators are defined as

$$F^{(-)} = h^{\mathrm{core}(-)} + \sum_j (2\,J_j^{(-)} - K_j^{(-)}) + J_p^{(+-)} \tag{13}$$

and

$$F^{(+)} = h^{\mathrm{core}(+)} + 2\sum_j J_j^{(+-)} \; .$$

J_j and K_j are the usual electronic Coulomb and exchange operators associated with the *jth* molecular orbital; $J_p^{(+-)}$ is the positronic Coulomb operator,

$$J_p^{(+-)}(\underline{r}_i) = - \int \phi_p^*\,(\underline{r}_p)\,[1/r_{ip}]\,\phi_p\,(\underline{r}_p)\,d\tau_p \;;$$

and $J_j^{(+-)}$ is the operator providing the Coulomb potential seen by a positron due to an electron in the *jth* orbital,

$$J_j^{(+-)}(\underline{r}_p) = -\int \phi_j^*(\underline{r}_i)\,[1/r_{ip}]\,\phi_j(\underline{r}_i)\,d\tau_i\ .$$

For computational purposes, it is convenient to express the energy as

$$E = (1/2)\sum_{\mu,\nu} P_{\mu\nu}^{(-)}\,(H_{\mu\nu}^{(-)} + F_{\mu\nu}^{(-)}) + (1/2)\sum_{\mu,\nu} P_{\mu\nu}^{(+)}\,(H_{\mu\nu}^{(+)} + F_{\mu\nu}^{(+)})\ , \tag{14}$$

where all matrix elements are in the basis set of atomic orbitals. It should also be noted that in forming the wavefunction (2) from the self-consistent solutions to Eqs. (12) we consistently employ the Aufbau Principle. That is, the $\underline{2n}$ electrons are put into the $\underline{n}$ lowest lying electronic orbitals, and the positron is assumed to occupy the positron orbital of lowest orbital energy, ε_p.

C. Approximations and Parameterization

By using the zero-differential overlap approximation, the multi-centered interaction integrals are simplified so that

$$<\chi_\mu\chi_\nu|r_{12}^{-1}|\chi_\lambda\chi_\alpha> = <\chi_\mu\chi_\nu|r_{12}^{-1}|\chi_\mu\chi_\nu>\delta_{\mu\lambda}\delta_{\nu\alpha} = \gamma_{\mu\nu}\delta_{\mu\lambda}\delta_{\nu\alpha} \tag{15}$$

and the Fock matrix elements become

$$F_{\mu\mu}^{(+)} = H_{\mu\mu}^{(+)} - \sum_{\lambda} P_{\lambda\lambda}^{(-)} \gamma_{\mu\lambda}$$

$$F_{\mu\nu}^{(+)} = H_{\mu\nu}^{(+)} \qquad (\mu \neq \nu)$$

$$\begin{aligned} F_{\mu\mu}^{(-)} &= H_{\mu\mu}^{(-)} - (1/2)\, P_{\mu\mu}^{(-)} \gamma_{\mu\mu} + \sum_{\lambda} P_{\lambda\lambda}^{(-)} \gamma_{\mu\lambda} \\ &\quad - \sum_{\lambda} P_{\lambda\lambda}^{(+)} \gamma_{\mu\lambda} \qquad (16) \\ F_{\mu\nu}^{(-)} &= H_{\mu\nu}^{(-)} - (1/2)\, P_{\mu\nu}^{(-)} \gamma_{\mu\nu} \; (\mu \neq \nu) \; . \end{aligned}$$

One of the CNDO approximations is to reduce Coulomb integrals to one per atom pair, i.e., $\gamma_{\mu\nu} = \gamma_{AB}$, where χ_μ is located on atom A and χ_ν on atom B.

It should be noted that the electron Fock matrix contains a contribution of the form, $-P_{\mu\nu}^{(-)} \gamma_{\mu\nu}/2$ and that this term is absent in the corresponding $F_{\mu\nu}^{(+)}$. This exchange term arises from the two-electron repulsions; since our system contains only one positron, this term does not appear in the positron matrix.

Eqs. (12) can now be solved by iterative techniques and the electron and positron wave functions can be obtained in which the electronic orbitals have been altered by the presence of the positron, and the positron orbital has been altered by the electrons.

The diagonal positron core matrix elements are approximated as

$$H_{\mu\mu}^{(+)} = U_{\mu\mu}^{(+)} + \sum_{B \neq A} Z_B \gamma_{AB} \; ; \quad (\chi_\mu \text{on atom A}) \qquad (17)$$

$U^{(+)}_{\mu\mu}$ is an atomic term containing the kinetic energy and potential energy of the positron in the field of the A<u>th</u> core; the second term describes the positron interactions with the other atomic cores.

The CNDO/2 parameterization as described by Pople and Beveridge[73] is used for all electron terms. However, for the positron no data such as ionization potentials and positron affinities are available. In order to parametrize the positron Fock terms we relate them to the corresponding electronic integrals as follows. For kinetic energy (T) and potential energy (V) matrix elements,

$$T^{(+)}_{\mu\nu} = T^{(-)}_{\mu\nu} \qquad \text{and} \qquad V^{(+)}_{\mu\nu} = - V^{(-)}_{\mu\nu} \tag{18}$$

so that

$$U^{(+)}_{\mu\mu} = T^{(+)}_{\mu\mu} + V^{(+)}_{\mu\mu} = T^{(-)}_{\mu\mu} - V^{(-)}_{\mu\mu} \tag{19}$$

Applying the virial theorem,

$$T^{(-)}_{\mu\mu} = - (1/2)\, V^{(-)}_{\mu\mu} = - U^{(-)}_{\mu\mu} \quad . \tag{20}$$

We see that

$$U^{(+)}_{\mu\mu} = - 3\, U^{(-)}_{\mu\mu} \quad . \tag{21}$$

Treatment of the off-diagonal core terms is not as direct. Because of the empirical nature of the bonding parameters, $\beta^{o(-)}_{AB}$, used by Pople and Beveridge, no direct conversion to

$\beta^{o(+)}_{AB}$ was found. Therefore, we decided to combine the Wolfsberg-Helmholtz approximation[74] with the ideas of Cusachs and Cusachs.[75] For the electronic core Hamiltonian matrix, we have

$$H^{(-)}_{\mu\nu} = T^{(-)}_{\mu\nu} + V^{(-)}_{\mu\nu} \tag{22a}$$

$$\approx k^{(-)}\, S_{\mu\nu}(H^{(-)}_{\mu\mu} + H^{(-)}_{\nu\nu})/2 \tag{22b}$$

$$\approx S_{\mu\nu}(2-|S_{\mu\nu}|)(H^{(-)}_{\mu\mu} + H^{(-)}_{\nu\nu})/2 \ . \tag{22c}$$

The analogous expressions for the positron are

$$H^{(+)}_{\mu\nu} = T^{(+)}_{\mu\nu} + V^{(+)}_{\mu\nu} \tag{23a}$$

$$\approx k^{(+)}\, S_{\mu\nu}(H^{(+)}_{\mu\mu} + H^{(+)}_{\mu\nu})/2 \tag{23b}$$

The terms in Eq. (23a) are now treated by the method of Cusachs and Cusachs:

$$T^{(+)}_{\mu\nu} \approx S_{\mu\nu}|S_{\mu\nu}|(T^{(+)}_{\mu\mu} + T^{(+)}_{\nu\nu})/2,$$

$$V^{(+)}_{\mu\nu} \approx S_{\mu\nu}(V^{(+)}_{\mu\mu} + V^{(+)}_{\nu\nu})/2,$$

and, substituting Eqs. (18) into the analogue of Eq. (19), yields

$$H^{(+)}_{\mu\mu} = (3/2)\, V^{(+)}_{\mu\mu} = 3T^{(+)}_{\mu\mu} \quad .$$

This gives directly

$$H^{(+)}_{\mu\nu} \simeq (1/3)\ S_{\mu\nu}(2 + |S_{\mu\nu}|)(H^{(+)}_{\mu\mu} + H^{(+)}_{\nu\nu})/2\ . \qquad (23c)$$

Values typically used[76] for the Wolfsberg-Helmholtz $k^{(-)}$ in Eq. (22b) range from 1.75 to 2.0, and comparison with (22c) shows that this corresponds to a range of $|S_{\mu\nu}|$ between 0 and 0.25. When these values are employed in Eq. (23c) and the result equated to (23b), it appears that $k^{(+)}$ should be in the range 2/3 to 3/4.

A computer program, PSCF, was developed by modifying the CNDO/2 program listed by Pople and Beveridge.[73] A listing of the pertinent subroutines is given in Section E of Appendix II. Along with the other approximations already described, we employed Eq. (23b) for $H^{(+)}_{\mu\nu}$ and varied $k^{(+)}$ over the indicated range.

D. Results

Using this formalism, we have studied the stability of positron and positronium complexes of benzene and a number of substituted benzene derivatives. In the process of carrying out the iterations to self-consistency, two slight problems arose. A number of calculations, especially with the larger values of $k^{(+)}$, oscillated rather than converging directly to an energy minimum. The oscillations were successfully eliminated by taking the modified density matrices and averaging the new calculated matrices with the old ones on each iteration. Also, for some of the symmetric molecules, the symmetry was lost during the iteration process. We believe that this resulted from round-off errors in the positron density matrix, where the elements are generally quite small. To eliminate the need for symmetry projection, we restricted our solutions to the symmetric cases by symmetrizing the molecular orbitals at each iteration.

The important results are listed in Tables IV and V for the two limiting values of $k^{(+)}$ mentioned previously. All calculations indicated that the positron should be bound by these molecules. Two approximations for the positron binding energies are given: $(-\varepsilon_p)$ is the negative of the positron orbital energy, and provides a Koopmans' theorem[77] estimate; the other entry (B.E.) was a direct calculation of the binding energy as the difference between the total energy of the neutral molecule and that of the positron-molecule complex. The two estimates are fairly comparable to one another, but the former is always of greater magnitude than the latter. The calculated positron binding energy depends critically on the value used for $k^{(+)}$. This is illustrated graphically in Fig. 32, which shows the two estimates of the positron affinity of nitrobenzene as a function of $k^{(+)}$. Corresponding to this, the number of bound positronium orbitals also increased with $k^{(+)}$. For the majority of the complexes, we found one or two bound orbitals for $k^{(+)} = 2/3$, and six to eight for $k^{(+)} = 3/4$.

Table IV. Positron and Positronium Binding Energies, a.u. (C) $k^{(+)} = 2.3$

Compound	$-\varepsilon_p$	B.E.(e^+)	e^+ site(a)	B.E.(Ps)
Benzene	0.0082	0.0081	C-H	-0.2197
Toluene	0.1877	0.1427	Alpha C-H	-0.0608
Fluorobenzene	0.2083	0.1030	Para C-H	-0.0809(b)
Aniline	0.3375	0.2736	N-H	+0.1184(b)
Benzonitrile	0.0780	0.0371	Meta C-H	-0.1726
Benzaldehyde	0.2256	0.1234	Carbonyl C-H	-0.0002
Nitrobenzene	0.0608	0.0200	Meta C-H	-0.1512
p-Benzoquinone	0.0213	0.0131	C-H	-0.0232

(a) greater than 90% of the e^+ charge density occurs here

(b) LUMO of the positronium complex is a σ orbital; in all other cases it is a π orbital.

(c) 1 a.u. = 27.21 eV = 627.71 kcal/mole.

Table V, Positron and Positronium Binding Energies, a.u. (C) $k^{(+)} = 3/4$

Compound	$-\varepsilon_p$	B.E.(e^+)	e^+ site[(a)]	B.E.(Ps)
Benzene	+0.2840	+0.2831	C-H	+0.0597
Toluene	+0.4717	+0.4270	Alpha C-H	+0.2225
Fluorobenzene	+0.4426	+0.3451	Para C-H	+0.1582[(b)]
Aniline	+0.6528	+0.5890	N-H	+0.4339[(b)]
Benzonitrile	+0.3671	+0.3194	C≡N	+0.1573
Benzaldehyde	+0.4686	+0.3757	Carbonyl C-H	+0.2533
Nitrobenzene	+0.4268	+0.3250	Para C-H	+0.1740
p-Benzoquinone	+0.3137	+0.3084	C-H	+0.2802

(a) greater than 90% of the e^+ charge density occurs here

(b) LUMO of the positronium complex is a σ orbital; in all cases it is a π orbital.

(c) 1 a.u. = 27.21 eV = 627.71 kcal/mole.

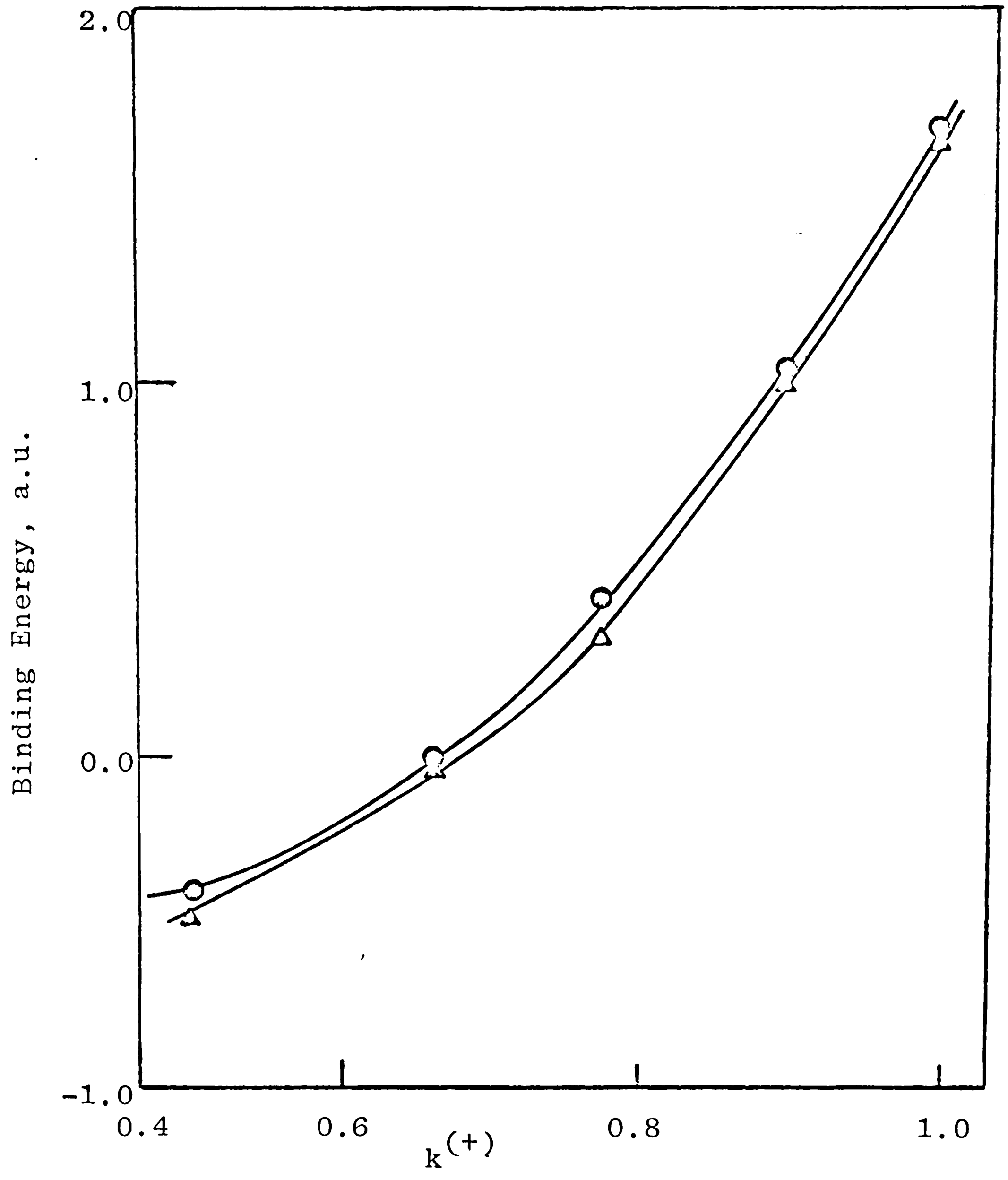


Figure 32. Variation in the Positron Binding Energy in Nitrobenzene with $k^{(+)}$. Koopman's Theorem Estimate (○) and Change in Energy Directly Calculated (△) for the Complex.

Also indicated in Tables IV and V are the locations of maximum positron density found for the several complexes. The positron was always found to be essentially localized in a single bond (or in equivalent bonds when this was required by symmetry). The position at which the positron was found varies widely through the series of molecules, and for some cases the positron's location was seen to change as $k^{(+)}$ was varied. We have not been able so far to reconcile these findings consistently with the results of Chapter 3. For example, if the complex formation is considered to be an example of nucleophilic attack, one might expect the positron to locate in the para position of nitrobenzene. This was observed for $k^{(+)} = 3/4$, but when $k^{(+)}$ was taken as 2/3, the positron moved to the meta position. Similar shifts were observed for benzonitrile, but for the larger $k^{(+)}$ the positron localized on the cyanide group. A number of additional points could be made, but at the present level of approximation extended discussion is probably not justified.

It is of some interest to note that the positron was always found to be most stable in a sigma rather than a pi molecular orbital. This is in fact expected if one looks at the positron's Fock matrix elements. In our approximations, all diagonal elements, $F^{(+)}_{\mu\mu}$, are positive, but the minimum values always occur for the hydrogen 1s orbitals. This situation could easily be expected to change if different approximations are employed.

Addition of the positron to a molecule is of course expected to cause some shifting of electronic charge density. As a typical case, we list in Table VI the calculated total atomic charge densities for the aniline molecule and its positron complex. The atomic charge density is obtained by summing the diagonal elements of the electronic charge-density and bond-order matrix (see Eq. (9)) over all the valence orbitals for each atom. The same data are shown graphically in slightly different form in Fig. 33. This shows profiles of net pi charge and net total charge before and after positron addition. The net total charge is the difference between the calculated charge density and the atomic core charge. The net pi charge is the pi-orbital density minus one. The figure is intended to show electron build-up at the various atoms; the numbers between the atoms are not meaningful. In all cases, the electron density is enhanced in the vicinity of the positron, as expected from the mutual attraction. The largest changes seen in the electron density upon positron addition were about 0.1 e, and most changes were appreciably less.

The positron densities listed in Table VI illustrate the high degree of localization found for the positron as indicated earlier. In this case, more than 99% of the total positron density is located in the NH_2 group.

Table VI. Calculated Total Charge Densities for Aniline and a Positron-Aniline Complex

$k^{(+)} = 3/4$

Atom	Charge Density in Molecule	Charge Density in Complex Electron	Positron
N	5.214	5.342	0.194
H_N	0.939	1.041	0.399
C_{SUBST}	3.770	3.789	0.002
C_{ORTHO}	4.010	3.971	0.001
H_{ORTHO}	1.057	1.032	0.001
C_{META}	3.912	3.897	0.000
H_{META}	1.066	1.014	0.000
C_{PARA}	3.982	3.942	0.000
H_{PARA}	1.064	1.016	0.000

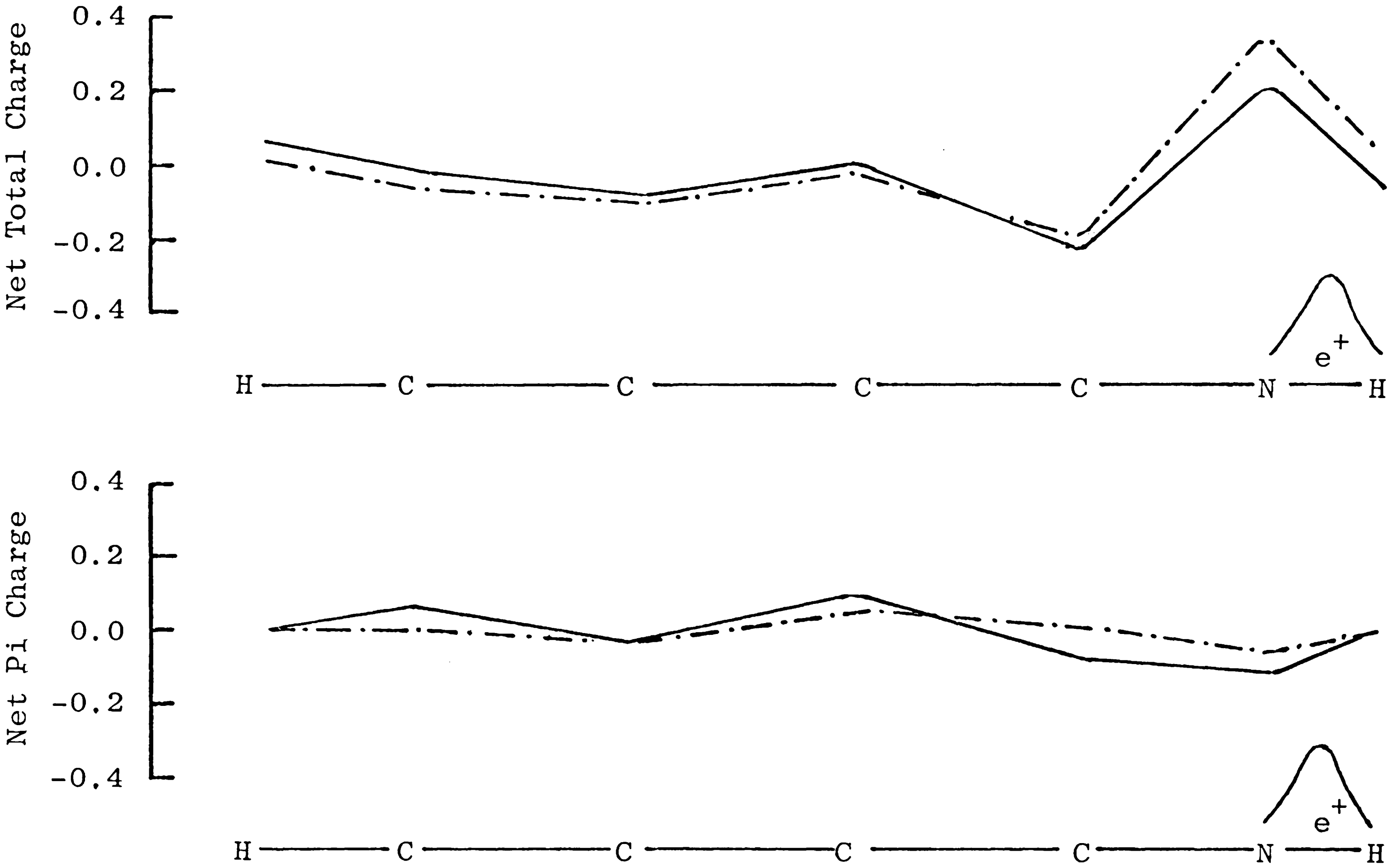


Figure 33. Profiles of Electronic Total Charge and Pi Charge for Aniline, Before (—) and After(-·-) Positron Addition. The Position of the Highest Positron Density (not to scale) is Indicated in the N-H Bond.

It is possible to estimate positronium binding energies for the molecules considered. This is done by considering the following cycle of processes, in which M denotes a neutral molecule, and Ps indicates the positronium atom (e^+e^-):

$$\begin{tikzcd}
\mathrm{Ps} + \mathrm{M} \arrow[r, "-\mathrm{B.E.}\ (\mathrm{PS})"] \arrow[d, "6.8\ \mathrm{eV} = 0.25\ \mathrm{a.u.}"'] & \mathrm{PsM} \\
e^+ + e^- + \mathrm{M} \arrow[r, "-\mathrm{B.E.}\ (e^+)"'] & e^+\mathrm{M} + e^- \arrow[u, "-\ \mathrm{E.A.}(e^+\mathrm{M})"']
\end{tikzcd}$$

Thus, the positronium binding energy is approximately

$$\mathrm{B.E.}\ (\mathrm{Ps}) = \mathrm{B.E.}\ (e^+) + \mathrm{E.A.}(e^+\mathrm{M}) - 0.25\ \mathrm{a.u.} \qquad (24)$$

Here, B.E. (e^+) is the molecular positron affinity discussed earlier, E.A. (e^+M) is the electron affinity of the positron-molecule complex, obtained by Koopman's theorem from the orbital energy of the first unoccupied electronic orbital in the complex, and the last term is the dissociation energy of the ground state of the hydrogen-like positronium atom.[80] The values obtained from Eq. (24) are listed in Tables IV and V for each molecule.

These calculations do not unambiguously show whether these molecules form stable positronium complexes. For all but aniline, the PsM complex was found to be unstable with respect to dissociation to Ps + M when $k^{(+)} = 2/3$. But with $k^{(+)} = 3/4$, all positronium-molecule complexes were found to be stable.

Positronium complex formation in liquids is entirely consistent with the "free volume model" that is used to describe pickoff quenching and may be considered as a special case of it. In the "free volume model," the positronium is repelled by the lattice potential of the molecules of the liquid and forced to remain in the free volume. The pickoff annihilation rate is determined by the small amount of overlap between the wave functions of the positronium and the molecules of the liquid. In the case of nitroaromatic liquids, a free volume exists, they have a density, viscosity and surface tension that is similar to that of many nonreactive liquids. However, if complex formation occurs, as indicated by our present experimental and theoretical results, the positronium atom is not repelled by the molecules of the liquid but is incorporated into them. In this reversible complex, the positron occupies a molecular orbitals and is no longer associated with the electron of the positronium atom. The observed rapid annihilation rate in nitroaromatics is caused by the enhanced electron density at the positron while in the complex.

The calculations do not entirely agree with the experimental results of the previous chapter that showed complex formation for only two of the compounds studied, nitrobenzene and p-benzoquinone. Schrader is presently performing similar calculations for positronium complexes[81] and he also finds them to be bound but not quite as strongly. Other recent experimental studies[78,79] suggest that the heats of complexation are negative and on the order of a few kcal/mole. This apparent discrepency could be caused by any number of reasons. Inaccurate parameterization of the PSCF program is one possibility. The calculations were only for a 1:1 complex and in solution this is not necessarily the case especially if one is to use the "free volume model." More results are needed for gas phase reactions in order to properly test our calculations.

CONCLUSIONS

A. Summary

The mechanism for the rapid chemical reaction of ortho-positronium with a nitroaromatic molecule, M, in solution was found to be

$$\mathrm{Ps} + \mathrm{M} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{PsM} \xrightarrow{k_2} \mathrm{M} + 2\gamma$$

The annihilation step is preceeded by reversible complex formation. Only diamagnetic compounds that form strong molecular complexes were found to react by this mechanism.

Nitroaromatics are known to be strong electron accepting molecules and this is directly related to their ability to form these complexes. Because of this, substituents on the aromatic ring were found to affect the reactivity of these molecules toward the positronium atom. Nitroaromatics with electron withdrawing groups attached to the aromatic ring were found to form more stable complexes with positronium than those that contained electron donating ones.

The complexing ability of these molecules was found to be heavily dependent upon conjugation of the nitro group with the aromatic ring. Steric interactions that force the nitro group out of the plane of the ring caused the forward rate constant, k_1, to be reduced.

A solvent effect was observed for this mechanism. Polar solvents were more able to assist the reactants in reaching the transition state associated with the complex formation step as compared to non-polar ones.

The results of CNDO calculations regarding the stability of positron and positronium complexes with large organic molecules showed that these complexes should be stable. However, complex formation was predicted for molecules in which no complex formation was observed.

B. Future Possibilities

The results of angular correlation experiments using the nitroaromatics could be used to determine the type(s) of electrons that annihilate the positron. Experiments similar to those mentioned for hexane and decane could be used to locate the bond(s) that contain the annihilation electrons, i.e., C-C, C-H, C-N, or N-O.

Many improvements can be made concerning the approximations used in the molecular orbital calculation. For example, the basis set used to construct the positron molecular orbitals was by no means complete. Atomic positron wave functions could be calculated and used here. These would also serve to better parameterize the calculations. These complexes were found to be stable in the absence of any external forces. Unlike the liquid phase, gas phase experiments should provide more realistic conditions under which the results of these calculations could be evaluated. Since positronium is formed above thermal energy, excited positronium complexes are also possible and configuration interaction (CI) calculations should be examined.

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APPENDIX I. Data Tables

A. Rate Constants for the Reaction of Ortho-Positronium with Aromatic Nitro Compounds in Benzene* at 295°K.

Solute k, $M^{-1}nsec^{-1}$	Concentration, mM	λ_2, $nsec^{-1}$	I_2, %
Nitrobenzene	1.62	0.376	37.0
27 ± 2	3.68	0.430	35.1
	6.73	0.511	34.7
	9.33	0.575	33.5
	11.56	0.653	34.3
p-Dinitrobenzene	1.52	0.417	36.5
50 ± 2	3.46	0.516	35.8
	6.35	0.669	36.8
	7.14	0.666	36.9
	10.90	0.882	36.4
	13.61	1.021	39.7
	15.87	1.141	38.5
m-Dinitrobenzene	1.38	0.391	35.0
47 ± 2	3.14	0.483	34.5
	5.77	0.605	34.7
	6.92	0.660	33.4
	8.56	0.697	33.0
	9.88	0.817	32.9
o-Dinitrobenzene	1.40	0.400	34.9
33 ± 2	2.70	0.453	32.5
	5.84	0.544	36.4
	8.09	0.650	29.5
	10.01	0.728	29.2
	13.48	0.841	28.6
	15.94	0.770	21.6
	20.45	0.997	26.4
p-Nitrobenzonitrile	2.71	0.450	36.1
39 ± 1	5.42	0.557	34.5
	8.12	0.667	35.4
	10.83	0.817	35.6
	13.54	0.879	35.8
	27.07	1.404	39.3

*Pure benzene has $\lambda_2 = 0.336$ $nsec^{-1}$ and $I_2 = 38.0\%$

Solute k, $M^{-1}nsec^{-1}$	Concentration, mM	λ_2, $nsec^{-1}$	I_2, %
m-Nitrobenzonitrile	2.58	0.434	35.1
39 ± 2	5.16	0.521	34.3
	7.74	0.636	33.5
	10.32	0.704	33.5
	12.91	0.830	35.6
	15.49	0.963	37.2
o-Nitrobenzonitrile	2.49	0.416	33.2
39 ± 2	4.97	0.476	29.7
	7.46	0.627	31.3
	9.94	0.722	31.8
	12.43	0.794	31.8
	14.92	0.917	33.2
m-Nitrobenzotrifluoride	1.88	0.403	36.8
	3.76	0.475	36.4
38 ± 1	7.52	0.605	35.6
	11.27	0.748	36.1
	15.03	0.911	38.7
	16.91	0.982	38.6
o-Nitrobenzotrifluoride	3.14	0.409	34.6
	6.27	0.501	32.4
25 ± 1	9.41	0.582	31.5
	12.54	0.644	30.4
	15.68	0.723	29.1
	18.82	0.810	28.3
p-Nitrobenzaldehyde	2.50	0.434	36.5
40 ± 2	4.99	0.533	34.6
	7.49	0.659	34.4
	9.99	0.743	34.5
	12.49	0.839	34.7
	14.98	0.936	35.1
m-Nitrobenzaldehyde	2.42	0.424	35.9
35 ± 1	4.84	0.506	36.2
	7.27	0.594	34.5
	9.69	0.679	35.0
	12.11	0.741	32.0
	14.53	0.860	35.0

Solute k, $M^{-1}nsec^{-1}$	Concentration, mM	λ_2, $nsec^{-1}$	I_2, %
o-Nitrobenzaldehyde 32 ± 2	3.00	0.428	35.3
	6.00	0.513	32.2
	9.00	0.614	31.7
	12.00	0.709	33.2
	15.00	0.800	33.8
	18.00	0.932	34.4
p-Nitroacetophenone 38 ± 2	2.52	0.411	33.0
	5.05	0.533	32.6
	7.57	0.626	31.2
	10.10	0.758	33.3
	12.62	0.803	28.6
	15.14	0.906	28.7
m-Nitroacetophenone 30 ± 2	2.32	0.401	35.9
	4.64	0.485	36.4
	6.96	0.546	33.9
	9.28	0.613	34.1
	11.61	0.701	34.4
	13.93	0.753	33.6
o-Nitroacetophenone 30 ± 2	2.88	0.412	34.4
	5.76	0.504	32.1
	8.64	0.599	31.3
	11.52	0.649	30.1
	14.40	0.736	27.8
	17.27	0.873	31.6
p-Nitrobenzoic acid 29 ± 5	0.17	0.349	37.9
	0.33	0.356	36.9
	0.50	0.357	37.2
	0.66	0.364	36.8
m-Nitrobenzoic acid 28 ± 2	4.35	0.481	35.9
	8.70	0.576	32.2
	13.05	0.694	32.9
	17.4	0.816	30.8
	26.1	1.092	32.2
o-Nitrobenzoic acid 20 ± 2	1.04	0.366	36.5
	2.60	0.399	34.5
	3.64	0.415	32.6
	5.20	0.428	33.0
	7.79	0.527	33.0
	10.39	0.538	29.8

Solute k, $M^{-1}nsec^{-1}$	Concentration, mM	λ_2, $nsec^{-1}$	I_2, %
p-Nitrotoluene	5.89	0.465	38.1
22 ± 2	11.60	0.580	33.9
	22.60	0.826	37.2
	29.45	0.972	34.4
m-Nitrotoluene	1.53	0.392	34.3
21 ± 2	5.62	0.487	35.0
	9.20	0.581	35.3
	16.95	0.743	35.1
	22.50	0.917	36.6
	33.75	1.018	29.7
o-Nitrotoluene	2.23	0.358	34.3
8.5 ± 2	4.24	0.360	32.0
	8.48	0.420	32.9
	12.72	0.455	32.0
	16.35	0.457	31.2
	23.10	0.515	29.9
2,6-Dimethylnitrobenzene	36.75	0.346	64.2
0.39 ± 0.05	73.50	0.372	60.5
	98.00	0.370	34.0
	110.25	0.370	33.1
	147.00	0.393	32.1
p-Nitroanisole	2.63	0.383	35.2
13 ± 2	5.25	0.396	35.1
	7.88	0.455	33.1
	10.51	0.477	33.9
	13.41	0.517	32.6
	15.76	0.549	32.2
m-Nitroanisole	3.33	0.420	36.4
27 ± 2	6.65	0.521	36.8
	9.98	0.580	34.7
	13.31	0.686	35.8
	16.63	0.762	35.6
	19.96	0.883	36.7
o-Nitroanisole	6.15	0.374	34.7
49 ± 8	12.30	0.411	33.0
	18.44	0.439	31.2
	24.59	0.449	27.5
	30.73	0.481	28.8
	36.88	0.532	28.6

Solute k, $M^{-1}nsec^{-1}$	Concentration, mM	λ_2, $nsec^{-1}$	I_2, %
p-Nitrophenol	1.47	0.351	37.0
13 ± 2	2.94	0.371	34.2
	5.87	0.406	33.4
	8.81	0.452	31.6
	11.74	0.468	32.3
	14.68	0.528	30.8
m-Nitrophenol	2.88	0.409	35.4
26 ± 2	5.76	0.486	34.2
	8.63	0.560	32.8
	11.51	0.623	33.6
	14.39	0.698	32.9
	17.27	0.802	33.2
o-Nitrophenol	3.17	0.438	36.7
33 ± 2	6.33	0.532	35.5
	9.62	0.635	36.1
	12.66	0.768	37.2
	15.83	0.876	37.0
	18.99	0.954	36.4
p-Nitro-N,N-dimethylaniline	2.41	0.381	35.9
	4.81	0.425	36.2
18 ± 2	7.21	0.463	34.8
	9.62	0.512	35.9
	12.02	0.551	35.2
	14.42	0.592	35.5
p-Nitroaniline	1.78	0.327	35.0
5.1 ± 0.6	2.62	0.355	36.3
	3.71	0.349	35.1
	4.58	0.369	35.1
	6.55	0.367	35.6
	6.85	0.376	34.2
	9.17	0.384	33.7
	10.28	0.372	33.5
	11.78	0.395	32.9
	13.10	0.394	33.0
	15.71	0.427	32.5
	18.33	0.421	31.5
m-Nitroaniline	1.62	0.362	36.9
19 ± 2	3.36	0.401	35.8
	6.20	0.454	33.9
	8.07	0.492	34.9
	9.31	0.529	33.1
	11.52	0.557	34.1
	13.44	0.586	33.3

Solute k, $M^{-1}nsec^{-1}$	Concentration, mM	λ_2, $nsec^{-1}$	I_2, %
o-Nitroaniline 10 ± 2	4.35	0.374	35.6
	8.70	0.415	34.2
	15.53	0.476	33.2
	21.76	0.521	32.0
	29.01	0.630	31.9
	36.26	0.643	31.6
	43.52	0.789	31.1
p-Nitrophenyl Acetate 26 ± 1	2.29	0.394	35.6
	4.59	0.459	33.7
	6.88	0.515	33.6
	9.17	0.569	34.3
	11.47	0.626	32.2
	13.76	0.698	32.4
o-Nitrophenyl Acetate 23 ± 1	2.47	0.388	35.5
	4.94	0.442	33.4
	7.41	0.497	32.2
	9.88	0.558	33.0
	12.35	0.619	32.7
	14.82	0.680	30.8
p-Nitrobenzyl alcohol 25 ± 1	1.37	0.372	37.0
	2.74	0.409	35.2
	5.49	0.469	33.3
	8.23	0.531	33.7
	10.98	0.600	32.3
	13.72	0.687	33.0
m-Nitrobenzyl alcohol 24 ± 2	2.97	0.432	35.6
	5.93	0.497	34.7
	8.90	0.542	33.2
	11.87	0.633	33.3
	14.84	0.681	31.7
	17.80	0.780	33.7
o-Nitrobenzyl alcohol 20 ± 2	2.99	0.401	34.2
	5.99	0.447	34.3
	8.98	0.507	32.0
	11.98	0.576	32.6
	14.97	0.638	32.9
	17.96	0.684	31.9

Solute k, $M^{-1}nsec^{-1}$	Concentration, mM	λ_2, $nsec^{-1}$	I_2, %
p-Nitrofluorobenzene 27 ± 2	2.36	0.397	36.1
	4.72	0.467	35.8
	7.07	0.531	36.2
	9.43	0.586	35.3
	11.79	0.654	35.3
	14.15	0.733	35.3
m-Nitrofluorobenzene 35 ± 2	2.35	0.415	35.5
	4.70	0.497	35.9
	7.05	0.573	34.7
	9.40	0.663	36.3
	11.75	0.743	35.3
	14.10	0.835	36.6
o-Nitrofluorobenzene 29 ± 2	2.36	0.407	36.0
	4.71	0.477	34.8
	7.07	0.522	32.7
	9.42	0.606	33.9
	11.78	0.667	33.4
	14.13	0.762	34.1
p-Nitrochlorobenzene 31 ± 2	1.65	0.380	36.4
	3.44	0.433	36.4
	3.85	0.482	35.5
	6.89	0.507	33.5
	9.55	0.658	35.0
	11.82	0.698	35.4
m-Nitrochlorobenzene 35 ± 2	1.62	0.391	36.5
	3.69	0.424	33.2
	6.76	0.546	33.1
	9.36	0.609	34.9
	11.59	0.745	33.7
o-Nitrochlorobenzene 22 ± 2	1.44	0.369	36.4
	3.28	0.420	34.5
	6.02	0.479	33.4
	8.33	0.529	32.4
	10.32	0.596	32.9
p-Nitrobromobenzene 32 ± 2	2.48	0.410	35.0
	4.96	0.492	33.7
	7.44	0.588	33.4
	9.92	0.655	32.7
	12.40	0.762	30.5
	14.88	0.782	33.9

Solute k, $M^{-1}nsec^{-1}$	Concentration, mM	λ_2, nsec	I_2, %
m-Nitrobromobenzene 36 ± 2	3.33	0.446	33.5
	6.66	0.536	31.9
	9.98	0.712	34.3
	13.31	0.814	33.6
	16.63	0.923	34.9
	19.96	1.048	36.8
o-Nitrobromobenzene 22 ± 2	1.48	0.374	34.1
	2.95	0.418	33.2
	5.90	0.481	32.3
	8.85	0.560	29.4
	11.80	0.583	30.5
	14.75	0.680	31.3
p-Nitroiodobenzene 32 ± 2	2.05	0.418	35.8
	4.10	0.476	34.6
	8.19	0.634	34.2
	10.24	0.691	33.2
	12.29	0.729	31.4
	14.34	0.796	32.0
m-Nitroiodobenzene 35 ± 2	3.06	0.410	33.1
	6.11	0.505	31.4
	9.17	0.587	30.5
	12.22	0.635	28.2
	15.28	0.722	30.9
	18.34	0.753	28.8
o-Nitroiodobenzene 23 ± 2	2.79	0.443	34.8
	5.58	0.519	33.0
	8.38	0.610	30.9
	11.17	0.756	34.1
	13.96	0.789	30.3
	16.75	0.945	34.1

B. Rate Constants for the Reaction of Ortho-Positronium with Aliphatic Nitro Compounds in Benzene at 295°K.

Solute 10^{-7} k, $M^{-1}sec^{-1}$	Concentration, M	λ_2, $nsec^{-1}$	I_2, %
Nitromethane	1.23	0.374	25.1
1.4 ± 0.3	2.47	0.383	19.2
	3.70	0.407	16.5
	4.96	0.426	14.8
	6.27	0.462	13.6
	8.64	0.464	12.1
Nitroethane	0.46	0.362	30.9
2.4 ± 0.3	0.93	0.364	27.1
	1.87	0.383	21.7
	2.80	0.420	18.8
	3.73	0.447	16.9
	4.67	0.451	14.8
	6.53	0.500	12.7
	8.40	0.510	12.0
1-Nitropropane	0.38	0.355	28.2
2.0 ± 0.3	1.50	0.363	21.4
	2.25	0.387	20.4
	3.00	0.398	17.2
	4.50	0.435	15.7
	5.25	0.454	14.1
	6.00	0.473	13.4
2-Nitropropane	0.14	0.343	36.4
1.85 ± 0.2	0.37	0.345	32.5
	1.11	0.358	24.9
	2.22	0.376	18.7
	4.45	0.430	15.1
	6.68	0.464	12.4
	8.91	0.499	10.9
	11.14	0.551	9.5
α-Nitrotoluene	0.85	0.432	19.0
0.11 ± 0.02	1.70	0.516	15.7
	2.55	0.619	13.6
	3.40	0.741	15.0
	8.46	1.235	10.3

C. Temperature Dependence of the Observed Rate Constants for the Reaction of Ortho-Positronium with Substituted Nitrobenzenes.

Solvent: Toluene

Solute	T, ^{o}C	λ_2, nsec^{-1}	I_2, %	k, M^{-1}nsec^{-1}
9.77 mM Nitrobenzene	-75	0.433	27.3	5.1
	-27	0.497	29.9	14.6
	5	0.567	32.7	23.9
	21	0.575	33.3	25.8
	23	0.594	32.2	27.9
	33	0.579	31.5	27.1
	38	0.576	33.8	27.0
	42	0.597	34.6	29.6
	56	0.531	34.2	23.7
	58	0.511	34.5	21.8
	75	0.436	36.2	15.3
	77	0.434	35.3	15.1
	93	0.340	37.2	6.6
	100	0.310	36.9	4.0
	113	0.292	37.3	3.1
	122	0.277	37.6	2.2
	129	0.270	38.4	1.9
	142	0.257	38.5	1.5
	154	0.244	39.4	1.0
7.36 mM p-Dinitrobenzene	-75	0.430	33.3	6.0
	-45	0.459	32.4	12.7
	-26	0.507	32.4	20.8
	5	0.595	32.4	35.6
	21	0.700	34.9	51.3
	35	0.752	35.3	59.5
	54	0.819	35.0	70.4
	70	0.927	36.5	86.5
	85	1.043	40.0	103.6
	105	1.125	40.9	116.5
	123	1.262	46.0	136.7
	149	1.231	46.5	134.8
	163	1.046	46.8	111.0
	173	0.856	44.4	86.1

Solute	T, ^oC	λ_2, $nsec^{-1}$	I_2, %	k, $M^{-1}nsec^{-1}$
2.02 mM p-Nitrobenzonitrile	-75	0.396	35.4	5.2
	6	0.400	34.2	33.5
	21	0.402	34.4	39.5
	40	0.418	34.5	53.4
	56	0.428	33.8	63.8
	71	0.447	35.8	77.8
	87	0.441	34.9	80.2
	95	0.434	36.2	79.5
	102	0.441	36.6	85.0
	117	0.437	36.8	88.2
	132	0.397	38.1	72.9
	152	0.350	40.0	56.5
	176	0.267	41.1	23.0
16.12 mM p-Nitroanisole	-75	0.444	27.1	3.9
	-45	0.510	28.9	8.9
	-26	0.530	30.2	11.0
	6	0.538	31.1	12.8
	23	0.466	36.6	9.0
	38	0.416	33.0	6.5
	54	0.353	35.1	3.3
	71	0.318	37.2	1.8
	86	0.296	36.3	1.0
	107	0.282	37.0	1.0
	130	0.262	38.6	0.7
	146	0.254	38.9	0.8
	173	0.235	40.3	0.8
13.22 mM p-Nitroaniline	5	0.385	28.6	3.9
	5	0.376	30.1	3.2
	21	0.359	32.2	2.8
	38	0.337	34.1	2.0
	59	0.319	36.0	1.6
	77	0.304	37.6	1.4
	96	0.295	38.2	1.7
	111	0.277	37.4	1.0
	128	0.268	38.7	1.2
	145	0.254	38.8	1.0
	160	0.242	39.2	0.2

Solute	T, °C	λ_2, nsec^{-1}	I_2, %	k, $M^{-1}\text{nsec}^{-1}$
206. mM 2,6-Dimethylnitrobenzene	-75	0.601	11.8	1.04
	-40	0.587	14.3	1.10
	-27	0.550	17.4	0.95
	5	0.419	27.8	0.42
	21	0.364	31.1	0.20
	37	0.342	32.8	0.15
	56	0.324	35.0	0.12
	74	0.307	35.7	0.09
	91	0.284	35.8	0.04
	106	0.277	36.8	0.05
	117	0.273	35.8	0.07
	130	0.261	36.5	0.05
	142	0.261	36.7	0.09
Miscellaneous				
13.15 mM p-Benzoquinone	-75	0.435	33.3	3.7
	5	0.725	33.7	29.8
	23	0.846	37.3	39.9
	41	1.035	43.1	55.2
	58	1.014	38.7	54.4
	78	1.193	48.5	69.0
1.315 mM p-Benzoquinone	-75	0.390	38.9	2.8
	5	0.367	36.4	25.8
	22	0.372	37.1	37.6
	46	0.373	37.7	51.2
	62	0.369	37.3	56.0
	82	0.369	38.3	66.2
	100	0.383	38.8	85.7
	123	0.382	42.4	96.6
	142	0.397	42.6	117.7
	157	0.374	43.1	107.2
	174	0.337	43.3	87.8
	192	0.263	47.1	40.4

Solvent: n-Heptane

Solute	T, ^oC	λ_2, $nsec^{-1}$	I_2, %	k, $M^{-1}nsec^{-1}$
19.55 mM Nitrobenzene	-75	0.425	27.0	4.9
	-42	0.589	28.8	14.3
	-26	0.608	32.0	15.8
	6	0.443	33.7	8.3
	21	0.335	35.0	3.3
	35	0.294	35.9	1.6
	44	0.277	36.1	1.0
	65	0.253	36.7	0.5
	86	0.237	36.7	0.3
1.814 mM p-Dinitrobenzene	22	0.403	33.8	73.0
	22	0.411	33.5	77.6
	38	0.422	34.3	88.8
	58	0.432	35.0	100.8
	76	0.456	35.9	120.4
	97	0.430	48.0	112.9
	122	0.297	50.8	49.1
	144	0.231	52.8	18.7
	161	0.198	52.5	6.2
26.75 mM p-Nitroanisole	5	0.305	35.6	0.92
	22	0.280	32.3	0.38
	22	0.279	33.6	0.34
	54	0.256	32.4	0.19
	76	0.240	40.0	0.08

Solvent: n-Pentanol

Solute	T, ^oC	λ_2 $nsec^{-1}$	I_2, %	k, $M^{-1}nsec^{-1}$
9.77 mM Nitrobenzene	-75	0.372	22.0	0.7
	5	0.406	21.1	8.3
	22	0.409	20.8	8.6
	37	0.428	21.0	10.6
	59	0.461	23.3	13.9
	82	0.461	23.3	14.6
	105	0.444	24.0	13.2
	127	0.392	23.8	8.0

Solute	T, °C	λ_2, $nsec^{-1}$	I_2, %	k, $M^{-1}nsec^{-1}$
7.72 mM p-Dinitrobenzene	-75	0.374	22.0	1.0
	5	0.414	19.9	11.6
	22	0.462	19.6	17.8
	40	0.516	20.6	24.9
	65	0.657	24.2	43.1
	88	0.758	27.3	56.9
	113	0.924	34.3	99.2
12.84 mM p-Nitroanisole	-75	0.371	37.2	0.5
	4	0.373	25.4	3.8
	22	0.379	21.0	4.3
	39	0.385	21.0	4.7
	59	0.378	21.5	4.1
	81	0.377	22.3	4.6
	101	0.359	23.4	3.4

D. Temperature Dependence of the Observed Rate Constants for the Reaction Ortho-Positronium with Solvents and Weakly Reactive Compounds.

Compound	T, °C	λ_2, $nsec^{-1}$	I_2, %	$10^{-7}k$, $M^{-1}\ sec^{-1}$
n-Heptane	-75	0.319	31.6	3.90
	-75	0.325	30.4	3.98
	-45	0.323	32.0	4.20
	-23	0.300	32.4	4.06
	6	0.286	34.8	4.09
	21	0.269	35.8	3.94
	21	0.263	36.1	3.86
	49	0.255	36.9	3.91
	65	0.248	37.8	3.91
	78	0.243	39.3	3.90
	92	0.224	39.1	3.68
	110	0.219	41.7	3.70
	131	0.208	41.5	3.61
	148	0.192	42.5	3.42
	162	0.184	42.9	3.34
	179	0.173	44.6	3.23
Toluene	-75	0.384	38.5	3.45
	-75	0.381	37.3	3.42
	-57	0.373	36.4	3.44
	-27	0.355	36.4	3.46
	3	0.333	37.3	3.43
	3	0.337	33.8	3.47
	21	0.319	36.8	3.39
	37	0.312	36.5	3.40
	53	0.303	36.2	3.38
	72	0.294	37.1	3.39
	91	0.277	37.8	3.28
	110	0.260	38.1	3.17
	136	0.250	40.5	3.17
	170	0.223	41.1	2.97
n-Pentanol	-75	0.366	23.6	3.97
	22	0.324	22.2	3.51
	22	0.326	22.8	3.53
	36	0.326	22.7	3.53
	65	0.325	22.9	3.52
	88	0.319	22.8	3.46
	108	0.315	23.1	3.42

Compound	T, ^{o}C	λ_2, $nsec^{-1}$	I_2, %	$10^{-7}k$, $M^{-1}\ sec^{-1}$
Benzonitrile	5	0.541	12.4	5.52
	23	0.458	10.5	4.67
	40	0.428	9.7	4.36
	67	0.457	12.2	4.66
	86	0.435	12.1	4.44
	112	0.443	14.0	4.52
	135	0.379	12.6	3.87
	157	0.379	13.8	3.86
2-Nitropropane	22	0.452	6.5	4.06
	41	0.481	8.1	4.31
	62	0.429	6.0	3.85
	91	0.447	9.0	4.01
	120	0.467	11.3	4.18

E. Thermodynamic Data for the Reactions of o-Ps

	Low Temperature Limit		High Temperature Limit
Compound	$E_a(1)$, kcal/mole	$\Delta S_a(-26^{o}C)$, eu*	$\Delta H_{EQ} + E_a(2)$, kcal/mole
Solvent: Toluene			
p-Nitroaniline	---	---	-1.1 ± 0.1
2,6-Dimethylnitrobenzene	---	---	-2.7 ± 0.3
p-Nitroanisole	0.9 ± 0.1	-10.2	-3.6 ± 0.3
Nitrobenzene	0.8 ± 0.1	-9.7	-4.5 ± 0.3
p-Nitrobenzonitrile	1.0 ± 0.1	-9.2	-6.0 ± 0.5
p-Dinitrobenzene	1.1 ± 0.1	-8.9	<-4.0
p-Benzoquinone	1.0 ± 0.1	-10.5	-7.5 ± 0.5
Solvent: n-Heptane			
p-Nitroanisole	---	---	-2.9 ± 0.4
Nitrobenzene	1.3 ± 0.3	-8.1	-4.4 ± 0.4
p-Dinitrobenzene	1.0 ± 0.2	-7.1	-8.0 ± 1.0
Solvent: n-Pentanol			
p-Nitroanisole	1.2 ± 0.1	-7.3	-1.3 ± 0.8
Nitrobenzene	1.3 ± 0.2	-6.2	-3.5 ± 0.6
p-Dinitrobenzene	1.8 ± 0.3	-5.5	---

* Calculated using the average $E_a(1)$ value.

APPENDIX II. Computer Programs

A. Introduction

Many trivial but time consuming calculations were performed by the three convenience programs (SLOW RATE, ARRHENIUS, AND HAMMETT) listed in this appendix. They are written in either FORTRAN (IV) or WATFIV for use on an autobatcher.

Section E contains the four subroutines needed to convert the CNDO/2 program listed in reference 68 into the PSCF program used to do the positron complex calculations. By substituting these four subroutines for the three (HUCKCL, SCFCLO, and CPRINT) in CNDO/2, one obtains the PSCF program.

The last section contains the program, PAL, that was used to calculate the lifetime, annihilation rate and intensity data from the positron lifetime spectra. The Colcomp output is generated in the POL subroutine of this program.

```
C         PROGRAM SLOW RATE
C
C         THIS FORTRAN(IV) PROGRAM CALCULATES RATE CONSTANTS FOR THE
C         REACTIONS OF O-PS WHEN LO, THE SOLVENT ANNIHILATION RATE,
C         CHANGES DUE TO HIGH CONCENTRATIONS OF A LIQUID SOLUTE
C         IDEAL MIXING IS ASSUMED
C         THE EQUATION NECESSARY IS L2(V/MN+MS)=KS+FN(KN-KS)
C         A PLOT OF THE LEFT HAND SIDE VERSUS FN SHOULD PRODUCE A
C         STRAIGHT LINE WITH SLOPE=(KN-KS) AND Y-INTERCEPT=KS
C
      DIMENSION X(20), Y(20), VS(20), VN(20), COM(10), FS(20), FN(20)
      REAL KS,MDS,MS(20),MN(20),MDN,MWS,MWN
      READ (5,60) NCASE
C         NUMBER OF CASES INPUT
20    READ (5,70) (COM(I),I=1,10)
      WRITE (6,70) (COM(I),I=1,10)
      READ (5,60) N
C         NUMBER OF DATA POINTS
      READ (5,80) DN,MWN
C         DENSITY OF SOLUTE, GM/ML, MOLECULAR WEIGHT OF SOLUTE
      DO 30 I=1,N
      READ (5,80) X(I),Y(I)
C         MOLARITY OF SOLUTE, LAMBDA-2(TIMES 10(-9))
30    CONTINUE
      KS=2.963*10**(7)
C         RATE CONSTANT FOR PURE SOLVENT
      DS=0.87865
C         DENSITY OF PURE SOLVENT, GM/ML
      MWS=78.12
C         MOLECULAR WEIGHT OF THE SOLVENT
      MDS=DS/MWS
C         CONCENTRATION OF THE PURE SOLVENT
```

```
      MDN=DN/MWN                                                        SLOW 330
C        CONCENTRATICN OF THE PURE SOLUTE                               SLOW 340
      DO 40 I=1,N                                                       SLOW 350
      VN(I)=X(I)/(MDN*1000.)                                            SLOW 360
C        VOLUME OF SOLUTE IN 1ML OF SOLUTION                            SLOW 370
      VS(I)=1.0-VN(I)                                                   SLOW 380
C        VOLUME OF SOLVENT IN 1ML OF SOLUTION                           SLOW 390
      MN(I)=X(I)/1000.                                                  SLOW 400
C        MILLIMOLES OF SOLUTE                                           SLOW 410
      MS(I)=VS(I)*MDS                                                   SLOW 420
C        MILLIMOLES OF SOLVENT                                          SLOW 430
      FS(I)=MS(I)/(MS(I)+MN(I))                                         SLOW 440
C        MOLE FRACTION OF SOLVENT                                       SLOW 450
      FN(I)=1.0-FS(I)                                                   SLOW 460
C        MOLE FRACTICN OF SOLUTE                                        SLOW 470
      Y(I)=Y(I)/((MS(I)+MN(I))*1000.)                                   SLOW 480
      X(I)=FN(I)                                                        SLOW 490
40    CCNTINUE                                                          SLOW 500
C     A LINEAR LEAST SQUARES PROGRAM FOR N DATA POINTS                  SLOW 510
      SUMX=0.0                                                          SLOW 520
      SUMX2=0.0                                                         SLOW 530
      SUMXY=0.0                                                         SLOW 540
      SUMY=0.00                                                         SLOW 550
      DO 50 I=1,N                                                       SLOW 560
      PRINT , 'X=',X(I),'Y=',Y(I)                                       SLOW 570
      SUMX=SUMX+X(I)                                                    SLOW 580
      SUMX2=SUMX2+X(I)**2                                               SLOW 590
      SUMXY=SUMXY+X(I)*Y(I)                                             SLOW 600
50    SUMY=SUMY+Y(I)                                                    SLOW 610
      SLOPE=(N*SUMXY-SUMX*SUMY)/(N*SUMX2-SUMX**2)                       SLOW 620
      YINTR=(SUMX2*SUMY-SUMX*SUMXY)/(N*SUMX2-SUMX**2)                   SLOW 630
      SLOPE=(SLOPE*10**9)                                               SLOW 640
```

```
      YINTR=(YINTR*10**9)
C        RATE CONSTANT OF THE SOLVENT, USE AS A CHECK
      SLOPE=SLOPE+KS
C        RATE CONSTANT OF THE SOLUTE
      WRITE (6,90) SLOPE,YINTR
      NCASE=NCASE-1
      IF (NCASE.LE.0) STOP
      GO TO 20
C
C
60    FORMAT (I2)
70    FORMAT (2X,10A4)
80    FORMAT (2F9.4)
90    FORMAT (20X,13H   K(SOLUTE)=,E11.3,13H  K(SOLVENT)=,E11.3)
      END
```

```
C          PROGRAM ARRHENIUS                                             ARHN  10
C                                                                        ARHN  15
C          THIS FORTRAN(IV) PROGRAM CALCULATES POINTS ON AN ARRHENIUS    ARHN  20
C          PLOT FROM O-PS ANNIHILATION RATES                             ARHN  30
C                                                                        ARHN  40
       REAL L2,L0,K,LOGK                                                 ARHN  50
       DIMENSION L2(50), L0(50), TC(50), TK(50), TKINV(50), IDENT(20)    ARHN  60
       DIMENSION K(50), LOGK(50)                                         ARHN  70
       DIMENSION CCN(50)                                                 ARHN  80
       READ (5,60) NCASE                                                 ARHN  90
C          NUMBER OF CASES INPUT                                         ARHN 100
       NCASE1=NCASE                                                      ARHN 110
20     READ (5,90) IDENT                                                 ARHN 120
C          IDENTIFIED, ONE FOR EACH CASE                                 ARHN 130
       WRITE (6,50)                                                      ARHN 140
       WRITE (6,90) IDENT                                                ARHN 150
       READ (5,60) N                                                     ARHN 160
C          NUMBER OF DATA POINTS FOR EACH CASE                           ARHN 170
       READ (5,70) CONC                                                  ARHN 180
C          CONCENTRATION OF SOLUTE IN MOLAR UNITS                        ARHN 190
       WRITE (6,100)                                                     ARHN 200
       DO 30 I=1,N                                                       ARHN 210
       READ (5,80) L2(I),TC(I)                                           ARHN 220
C          LAMBDA-2, CENTIGRADE TEMPERATURE                              ARHN 230
C          L2 TIMES 10(-9)                                               ARHN 240
       L0(I)=0.28397-(0.0006005*TC(I))                                   ARHN 250
C          TEMPERATURE DEPENDENCE OF SOLVENT ANNIHILATION RATE           ARHN 260
       TK(I)=TC(I)+273.                                                  ARHN 270
C          KELVIN TEMPERATURE                                            ARHN 280
       K(I)=(L2(I)-L0(I))/CONC                                           ARHN 290
C          OBSERVED RATE CONSTANT                                        ARHN 300
C          K EXPRESSED TIMES 10(-9)                                      ARHN 310
```

```
      TKINV(I)=1000.0/TK(I)
C        INVERSE KELVIN TEMPERATURE TIMES 1000
30    CONTINUE
      DO 40 I=1,N
      WRITE (6,110) TC(I),L2(I),TKINV(I),K(I)
40    CONTINUE
      NCASE=NCASE-1
      IF (NCASE.NE.0) GO TO 20
      WRITE (6,50)
      STOP
C
C
C
50    FORMAT (1H1)
60    FORMAT (I2)
70    FORMAT (F12.9)
80    FORMAT (2F9.4)
90    FORMAT (20A4)
100   FORMAT (20X,43H       TC         L2     1000/TK  K*10(-9)  )
110   FORMAT (20X,F10.1,F10.4,F10.3,F10.4)
      END
```

```
C        PROGRAM HAMMETT
C
C        THIS PROGRAM CALCULATES POINTS ON A HAMMETT PLOT WHERE THE
C        HAMMETT EQUATION IS
C
C        LOG(K/KREF)=RHO(IND)*SIGMA(IND)+RHO(RES)*SIGMA(RES)
C
      REAL LOGY(100),LOGYC(100)
      REAL LOGYAV
      DIMENSION ID(20)
      DIMENSION SUB(100,9), SBAR(100)
      DIMENSION Y(100), SI(100), SR(100), YCAL(100), DEL(100)
      READ , NCASE
C        NUMBER OF CASES INPUT
20    READ (5,100) ID
C        IDENTIFIER, ONE FOR EACH CASE
      WRITE (6,120)
      WRITE (6,110) ID
      READ , N
C        NUMBER OF DATA POINTS
      DO 30 I=1,N
      READ (5,80) (SUB(I,J),J=1,9),Y(I),SI(I),SR(I)
C        SUBSTITUENT ON NITROBENZENE, KOBS,SIGMA(IND), SIGMA(RES)
C        Y(1) MUST BE FOR REFERENCE COMPOUND, I.E. NITROBENZENE
30    CONTINUE
      DO 40 I=1,N
      LOGY(I)=ALOG10(Y(I)/Y(1))
40    CONTINUE
C        LINEAR LEAST SQUARES PORTION OF THE PROGRAM
      SLYSI=0.0
      SLYSR=0.0
      SSRSI=0.0
```

```
      SSR2=0.0                                                          HMET 320
      SSI2=0.0                                                          HMET 330
      DO 50 I=1,N                                                       HMET 340
      SLYSI=SLYSI+LOGY(I)*SI(I)                                         HMET 350
      SLYSR=SLYSR+LOGY(I)*SR(I)                                         HMET 360
      SSRSI=SSRSI+SR(I)*SI(I)                                           HMET 370
      SSI2=SSI2+SI(I)*SI(I)                                             HMET 380
      SSR2=SSR2+SR(I)*SR(I)                                             HMET 390
50    CCNTINUE                                                          HMET 400
      SSRSI2=SSRSI**2                                                   HMET 410
      PI=((SSR2*SLYSI)-(SSRSI*SLYSR))/((SSI2*SSR2)-(SSRSI2))            HMET 420
C        RHO INDUCTIVE                                                  HMET 430
      PR=((SSI2*SLYSR)-(SSRSI*SLYSI))/((SSI2*SSR2)-(SSRSI2))            HMET 440
C        RHO RESONANCE                                                  HMET 450
      PRINT , 'P(I)=',PI,'P(R)=',PR                                     HMET 460
      PRINT , 'SUBST.  RATEK  RATEKCAL  DEL  LOGK/KNB  LOGK/KC  SBAR'   HMET 470
      DO 60 I=1,N                                                       HMET 480
      SBAR(I)=PI*SI(I)+PR*SR(I)                                         HMET 490
C        SIGMA BAR                                                      HMET 500
      YCAL(I)=10**(SBAR(I)+ALOG10(Y(1)))                                HMET 510
      LOGYC(I)=ALOG10(YCAL(I)/Y(1))                                     HMET 520
      DEL(I)=LOGYC(I)-LOGY(I)                                           HMET 530
C        DIFFERENCE BETWEEN LOG(K) AND LOG(KCALC)                       HMET 540
      WRITE (6,90) (SUB(I,J),J=1,9),Y(I),YCAL(I),DEL(I),LOGY(I),LOGYC(I)HMET 550
     1,SBAR(I)                                                          HMET 560
60    CCNTINUE                                                          HMET 570
      LOGYAV=0.0                                                        HMET 580
      DELAV=0.0                                                         HMET 590
      DO 70 I=1,N                                                       HMET 600
      DELAV=DELAV+DEL(I)**2                                             HMET 610
      LOGYAV=LOGYAV+LOGY(I)**2                                          HMET 620
70    CCNTINUE                                                          HMET 630
```

```
      SD=(DELAV/FLOAT(N))**0.5
C        STANDARD DEVIATION
      RMS=(LOGYAV/FLOAT(N))**0.5
C        ROOT MEAN SQUARE
      F=SD/RMS
C        EHRENSON'S FIT PARAMETER
      PRINT , 'STDDEV=',SD,'RMS=',RMS,'F=',F
      NCASE=NCASE-1
      IF (NCASE.NE.0) GO TO 20
      WRITE (6,120)
      STOP
C
80    FORMAT (9A1,3F10.5)
90    FORMAT (5X,9A1,6F10.4)
100   FORMAT (20A4)
110   FORMAT (10X,20A4)
120   FORMAT (1H1)
      END
```

```
C     PROGRAM PSCF

      SUBROUTINE HUCKCL(ICORE)
C     CALCULATIONS DONE IN THIS SUBROUTINE USE EXTENDED HUCKEL
C     THEORY FOR CLOSED SHELLS ONLY
C     OVERLAPS ARE IN MATRIX A,COULOMB INTEGRALS(GAMMA) ARE IN MATRIX G
C     A SUBROUTINE CORMOD(ICORE) MUST BE SUPPLIED.  THIS IS USED TO
C     MODIFY THE CORE INTEGRALS IF (ICORE.NE.0)
C     FOR MINDO, USE ICORE=2
      IMPLICIT REAL*8(A-H,O-Z)
      COMMON /ARRAYS/ A(80,80),B(80,80),PS(80,80),PSB(80,80)
      COMMON /INFO/ NATOMS,CHARGE,MULTIP,AN(35),C(35,3),N
      COMMON /INFO1/ CZ(35),U(80),ULIM(35),LLIM(35),NELECS,OCCA,OCCB
      COMMON /GAB/ XXX(400),G(35,35),Q(80),YYY(80),ENERGY,XXY(214)
      COMMON /OPTICM/ OPTION,OPNCLO,HUCKEL,CNDO,INDO,CLOSED,OPEN
      COMMON /CORE/ G1(18),F2(18),ENEG(18,3),BETA0(18)
      COMMON /PS/ PSQ(80),PSK
      INTEGER CHARGE,OCCA,OCCB,UL,AN,CZ,U,ULIM,ANI
      INTEGER OPTION,OPNCLO,HUCKEL,CNDO,INDO,CLOSED,OPEN
      G1(3)=.092012D0
      G1(4)=.1407D0
      G1(5)=.199265D0
      G1(6)=.267708D0
      G1(7)=.346029D0
      G1(8)=.43423D0
      G1(9)=.532305D0
      F2(3)=.049865D0
      F2(4)=.089125D0
      F2(5)=.13041D0
      F2(6)=.17327D0
      F2(7)=.219055D0
```

```
      F2(8)=.266415D0                                                   HUCK 300
      F2(9)=.31580D0                                                    HUCK 310
      ENEG(1,1)=7.1761D0                                                HUCK 320
      ENEG(3,1)=3.1055D0                                                HUCK 330
      ENEG(3,2)=1.258D0                                                 HUCK 340
      ENEG(4,1)=5.94557D0                                               HUCK 350
      ENEG(4,2)=2.563D0                                                 HUCK 360
      ENEG(5,1)=9.59407D0                                               HUCK 370
      ENEG(5,2)=4.001D0                                                 HUCK 380
      ENEG(6,1)=14.051D0                                                HUCK 390
      ENEG(6,2)=5.572D0                                                 HUCK 400
      ENEG(7,1)=19.31637D0                                              HUCK 410
      ENEG(7,2)=7.275D0                                                 HUCK 420
      ENEG(8,1)=25.39017D0                                              HUCK 430
      ENEG(8,2)=9.111D0                                                 HUCK 440
      ENEG(9,1)=32.2724D0                                               HUCK 450
      ENEG(9,2)=11.08D0                                                 HUCK 460
      ENEG(11,1)=2.804D0                                                HUCK 470
      ENEG(11,2)=1.302D0                                                HUCK 480
      ENEG(11,3)=0.150D0                                                HUCK 490
      ENEG(12,1)=5.1254D0                                               HUCK 500
      ENEG(12,2)=2.0516D0                                               HUCK 510
      ENEG(12,3)=0.16195D0                                              HUCK 520
      ENEG(13,1)=7.7706D0                                               HUCK 530
      ENEG(13,2)=2.9951D0                                               HUCK 540
      ENEG(13,3)=0.22425D0                                              HUCK 550
      ENEG(14,1)=10.0327D0                                              HUCK 560
      ENEG(14,2)=4.1325D0                                               HUCK 570
      ENEG(14,3)=0.337D0                                                HUCK 580
      ENEG(15,1)=14.0327D0                                              HUCK 590
      ENEG(15,2)=5.4638D0                                               HUCK 600
      ENEG(15,3)=0.500D0                                                HUCK 610
```

```
      ENEG(16,1)=17.6496D0                                              HUCK 620
      ENEG(16,2)=6.989D0                                                HUCK 630
      ENEG(16,3)=0.71325D0                                              HUCK 640
      ENEG(17,1)=21.5906D0                                              HUCK 650
      ENEG(17,2)=8.7081D0                                               HUCK 660
      ENEG(17,3)=0.97695D0                                              HUCK 670
      BETA0(1)=-9.D0                                                    HUCK 680
      BETA0(3)=-9.D0                                                    HUCK 690
      BETA0(4)=-13.D0                                                   HUCK 700
      BETA0(5)=-17.D0                                                   HUCK 710
      BETA0(6)=-21.D0                                                   HUCK 720
      BETA0(7)=-25.D0                                                   HUCK 730
      BETA0(8)=-31.D0                                                   HUCK 740
      BETA0(9)=-39.D0                                                   HUCK 750
      BETA0(11)=-7.7203D0                                               HUCK 760
      BETA0(12)=-9.4471D0                                               HUCK 770
      BETA0(13)=-11.3011D0                                              HUCK 780
      BETA0(14)=-13.065D0                                               HUCK 790
      BETA0(15)=-15.070D0                                               HUCK 800
      BETA0(16)=-18.150D0                                               HUCK 810
      BETA0(17)=-22.330D0                                               HUCK 820
      IF (ICORE.NE.0) CALL CORMOD (ICORE)                               HUCK 830
C     FIND NELECS AND FILL W CORE(DIAGONAL) WITH (I+A)/2                HUCK 840
      NELECS=0                                                          HUCK 850
      DO 50 I=1,NATOMS                                                  HUCK 860
      NELECS=NELECS+CZ(I)                                               HUCK 870
      LL=LLIM(I)                                                        HUCK 880
      UL=ULIM(I)                                                        HUCK 890
      ANI=AN(I)                                                         HUCK 900
      L=0                                                               HUCK 910
      DO 40 J=LL,UL                                                     HUCK 920
      L=L+1                                                             HUCK 930
```

```
      IF (L.EQ.1) GO TO 30                                              HUCK 940
      IF (L.LT.5) GO TO 20                                              HUCK 950
      A(J,J)=-ENEG(ANI,3)/27.21D0                                       HUCK 960
      PS(J,J)=-3.D0*(A(J,J)-(DFLOAT(CZ(I))-.5D0)*G(I,I))                HUCK 970
      GO TO 40                                                          HUCK 980
   20 A(J,J)=-ENEG(ANI,2)/27.21D0                                       HUCK 990
      PS(J,J)=-3.D0*(A(J,J)-(DFLOAT(CZ(I))-.5D0)*G(I,I))                HUCK1000
C     MINDO CORRECTION FOR P-ORBITALS                                   HUCK1010
      IF (ICORE.EQ.2) A(J,J)=A(J,J)+0.5D0*G(I,I)+G1(ANI)*(DFLOAT(CZ(I)-1HUCK1020
     1)/6.0D0-1.0D0)/3.0D0+F2(ANI)*(0.28D0/3.0D0*DFLOAT(CZ(I)-1)-0.08D0*HUCK1030
     2(DFLOAT(CZ(I))-2.5D0))                                            HUCK1040
      GO TO 40                                                          HUCK1050
   30 A(J,J)=-ENEG(ANI,1)/27.21D0                                       HUCK1060
      PS(J,J)=-3.D0*(A(J,J)-(DFLOAT(CZ(I))-.5D0)*G(I,I))                HUCK1070
C     MINDO CORRECTION FOR S-ORBITALS                                   HUCK1080
C     H ATOMS                                                           HUCK1090
      IF (ICORE.EQ.2.AND.ANI.EQ.1) A(J,J)=A(J,J)+0.5D0*G(I,I)           HUCK1100
C     OTHER ATOMS THAN H                                                HUCK1110
      IF (ICORE.EQ.2.AND.ANI.NE.1) A(J,J)=A(J,J)+0.5D0*G(I,I)+G1(ANI)/12HUCK1120
     1.0D0                                                              HUCK1130
   40 CONTINUE                                                          HUCK1140
   50 CONTINUE                                                          HUCK1150
      NELECS=NELECS-CHARGE                                              HUCK1160
      OCCA=NELECS/2                                                     HUCK1170
C     FORM HUCKEL HAMILTONIAN IN A (OFF DIAGONAL TWO CENTER TERMS)      HUCK1180
      DO 90 I=2,N                                                       HUCK1190
      K=U(I)                                                            HUCK1200
      L=AN(K)                                                           HUCK1210
      UL=I-1                                                            HUCK1220
      DO 90 J=1,UL                                                      HUCK1230
      KK=U(J)                                                           HUCK1240
      LL=AN(KK)                                                         HUCK1250
```

```
      IF ((L.GT.9).OR.(LL.GT.9)) GO TO 80                               HUCK1260
      IF (ICORE.NE.2) GO TO 60                                          HUCK1270
C     MINDO BETAS                                                       HUCK1280
      A(I,J)=A(I,J)*A(J,I)                                              HUCK1290
      GO TO 70                                                          HUCK1300
60    PS(I,J)=0.75D0*A(I,J)*(PS(I,I)+PS(J,J))/2.0D0                     HUCK1310
      A(I,J)=A(I,J)*(BETAO(L)+BETAO(LL))/54.42D0                        HUCK1320
      PS(J,I)=PS(I,J)                                                   HUCK1330
70    A(J,I)=A(I,J)                                                     HUCK1340
      GO TO 90                                                          HUCK1350
80    PS(I,J)=0.75D0*A(I,J)*(PS(I,I)+PS(J,J))/2.0D0                     HUCK1360
      A(I,J)=0.750D0*A(I,J)*(BETAO(L)+BETAO(LL))/54.42D0                HUCK1370
      PS(J,I)=PS(I,J)                                                   HUCK1380
      A(J,I)=A(I,J)                                                     HUCK1390
90    CONTINUE                                                          HUCK1400
C     OFF DIAG TERMS CALCD BY A WOLFSBERG-HELMHOLTZ METHOD               HUCK1410
      DO 100 I=1,N                                                      HUCK1420
100   Q(I)=A(I,I)                                                       HUCK1430
      RHO=1.D-8                                                         HUCK1440
      CALL EIGN (N,RHO)                                                 HUCK1450
C     EIGENVECTORS(IN B) ARE CONVERTED INTO DENSITY MATRIX(IN B)        HUCK1460
      CALL DEN (OCCA,2,N)                                               HUCK1470
C     ADD V(AB) TO HCORE--CNDO                                          HUCK1480
      DO 120 I=1,N                                                      HUCK1490
      J=U(I)                                                            HUCK1500
      Q(I)=Q(I)+0.5D0*G(J,J)                                            HUCK1510
      DO 110 K=1,NATOMS                                                 HUCK1520
      IF (K.EQ.J) GO TO 110                                             HUCK1530
      PS(I,I)=PS(I,I)+DFLOAT(CZ(K))*G(J,K)                              HUCK1540
110   Q(I)=Q(I)-DFLOAT(CZ(K))*G(J,K)                                    HUCK1550
      PSQ(I)=PS(I,I)                                                    HUCK1560
120   CONTINUE                                                          HUCK1570
```

```
C     EXIT SEGMENT IF ONLY CNDO APPROXIMATIONS ARE DESIRED              HUCK1580
      IF (OPTION.EQ.CNDO) GO TO 200                                     HUCK1590
C     INDO MODIFICATION(CORRECTION TO U(I,I))                           HUCK1600
      DO 190 I=1,NATOMS                                                 HUCK1610
      K=AN(I)                                                           HUCK1620
      J=LLIM(I)                                                         HUCK1630
      IF ((K.GT.1).AND.(K.LT.10)) GO TO 130                             HUCK1640
      GO TO 190                                                         HUCK1650
  130 IF (K.LE.3) GO TO 140                                             HUCK1660
      Q(J)=Q(J)+(DFLOAT(CZ(I))-1.5D0)*G1(K)/6.D0                        HUCK1670
  140 IF (K.EQ.3) GO TO 160                                             HUCK1680
      IF (K.EQ.4) GO TO 150                                             HUCK1690
      TEMP=G1(K)/3.D0+(DFLOAT(CZ(I))-2.5D0)*2.D0*F2(K)/25.D0            HUCK1700
      GO TO 170                                                         HUCK1710
  150 TEMP=G1(K)/4.D0                                                   HUCK1720
      GO TO 170                                                         HUCK1730
  160 TEMP=G1(K)/12.D0                                                  HUCK1740
  170 CONTINUE                                                          HUCK1750
      DO 180 L=1,3                                                      HUCK1760
  180 Q(J+L)=Q(J+L)+TEMP                                                HUCK1770
  190 CONTINUE                                                          HUCK1780
  200 CONTINUE                                                          HUCK1790
      DO 220 I=1,N                                                      HUCK1800
      DO 210 J=I,N                                                      HUCK1810
      PSB(I,J)=0.0D0                                                    HUCK1820
      PSB(J,I)=PSB(I,J)                                                 HUCK1830
  210 A(J,I)=A(I,J)                                                     HUCK1840
  220 A(I,I)=Q(I)                                                       HUCK1850
      WRITE (6,230)                                                     HUCK1860
      CALL SCFOUT (0,1)                                                 HUCK1870
      WRITE (6,240)                                                     HUCK1880
      CALL SCFOUT (0,3)                                                 HUCK1890
```

```
      WRITE (6,250)                                                     HUCK1900
      RETURN                                                            HUCK1910
C                                                                       HUCK1920
230   FORMAT (1X,28H ELECTRONIC CORE HAMILTONIAN/)                      HUCK1930
240   FORMAT (1X,29H POSITRONIC CORE HAMILTONIAN /)                     HUCK1940
250   FORMAT (1X,73H INITIAL ELECTRON DENSITY MATRIX AND EIGENVALUES CALHUCK1950
     1CULATED FROM HCORE(-)/)                                           HUCK1960
      END                                                               HUCK1970
```

```
      SUBROUTINE DEN (IOCC,MOP,N)                                       DENS  10
      IMPLICIT REAL*8(A-H,O-Z)                                          DENS  20
      COMMON /ARRAYS/ A(80,80,4)                                        DENS  30
      DIMENSION X(400)                                                  DENS  40
      L=1                                                               DENS  50
      IF (IOCC.GT.1) L=2                                                DENS  60
      DO 40 I=1,N                                                       DENS  70
      DO 20 J=I,N                                                       DENS  80
      X(J)=0.0D0                                                        DENS  90
      DO 10 K=1,IOCC                                                    DENS 100
 10   X(J)=X(J)+L*A(I,K,MOP)*A(J,K,MOP)                                 DENS 110
 20   CONTINUE                                                          DENS 120
      DO 30 J=I,N                                                       DENS 130
 30   A(I,J,MOP)=X(J)                                                   DENS 140
 40   CONTINUE                                                          DENS 150
      DO 50 I=1,N                                                       DENS 160
      DO 50 J=I,N                                                       DENS 170
 50   A(J,I,MOP)=A(I,J,MOP)                                             DENS 180
      RETURN                                                            DENS 190
      END                                                               DENS 200
```

```
      SUBROUTINE SCFCLO
C     CNDO/INDO CLOSED SHELL SCF SEGMENT
C     GAMMA MATRIX CONTAINED IN G, CORE HAMILTONIAN CONTAINED IN Q AND
C     UPPER TRIAMGLE OF A, AND INITIAL DENSITY MATRIX CONTAINED IN B
C     OPTIONS CNDO OR INDO
      IMPLICIT REAL*8(A-H,O-Z)
      COMMON /ARRAYS/ A(80,80),B(80,80),PS(80,80),PSB(80,80)
      COMMON /INFO/ NATOMS,CHARGE,MULTIP,AN(35),C(35,3),N
      COMMON /GAB/ XXX(400),G(35,35),Q(80),YYY(80),ENERGY,XXY(214)
      COMMON /INFO1/ CZ(35),U(80),ULIM(35),LLIM(35),NELECS,OCCA,OCCB
      COMMON /OPTICM/ OPTION,OPNCLO,HUCKEL,CNDO,INDO,CLOSED,OPEN
      COMMON /CORE/ G1(18),F2(18),ENEG(18,3),BETAO(18)
      COMMON /PS/ PSQ(80),PSK
      DIMENSION HELP1(80,80), HELP2(80,80), S(80,80), P(80,80)
      INTEGER OPTION,OPNCLO,HUCKEL,CNDO,INDO,CLOSED,OPEN
      INTEGER CHARGE,OCCA,OCCB,UL,ULIM,U,AN,CZ,Z
      Z=0
      IT=99
      RHO=1.D-8
      DO 20 I=1,N
      II=U(I)
      DO 20 K=1,N
      JJ=U(K)
20    PS(I,I)=PS(I,I)-B(K,K)*G(II,JJ)
      DO 30 I=1,N
      DO 30 J=1,N
      HELP1(I,J)=A(I,J)
      HELP2(I,J)=B(I,J)
      A(I,J)=PS(I,J)
30    B(I,J)=PSB(I,J)
      CALL EIGN (N,RHO)
      CALL DEN (1,2,N)
```

```
      WRITE (6,230)
      CALL SCFOUT (1,2)
      DO 40 I=1,N
      DO 40 J=1,N
      PS(I,J)=A(I,J)
      PSB(I,J)=B(I,J)
      A(I,J)=HELP1(I,J)
40    B(I,J)=HELP2(I,J)
50    CONTINUE
      Z=Z+1
      ENERGY=0.0D0
      DO 60 I=1,N
      A(I,I)=Q(I)
      PS(I,I)=PSQ(I)
      DO 60 J=I,N
      S(I,J)=B(I,J)
      S(J,I)=S(I,J)
      P(I,J)=PSB(I,J)
      P(J,I)=P(I,J)
60    A(J,I)=A(I,J)
      DO 70 I=1,N
      II=U(I)
      A(I,I)=A(I,I)-B(I,I)*G(II,II)*0.5D0
      DO 70 K=1,N
      JJ=U(K)
      PS(I,I)=PS(I,I)-B(K,K)*G(II,JJ)
70    A(I,I)=A(I,I)+B(K,K)*G(II,JJ)-PSB(K,K)*G(II,JJ)
      NM=N-1
      DO 80 I=1,NM
      II=U(I)
      LL=I+1
      DO 80 J=LL,N
```

```
      JJ=U(J)
80    A(J,I)=A(J,I)-B(J,I)*G(II,JJ)*0.5D0
C     INDO MODIFICATION
      IF (OPTION.EQ.CNDO) GO TO 110
      DO 100 II=1,NATOMS
      K=AN(II)
      I=LLIM(II)
      IF (K.EQ.1) GO TO 100
      PAA=B(I,I)+B(I+1,I+1)+B(I+2,I+2)+B(I+3,I+3)
      A(I,I)=A(I,I)-(PAA-B(I,I))*G1(K)/6.D0
      DO 90 J=1,3
      A(I+J,I+J)=A(I+J,I+J)-B(I,I)*G1(K)/6.D0-(PAA-B(I,I))*7.D0*F2(K)/50
     1.D0+B(I+J,I+J)*11.D0*F2(K)/50.D0
90    A(I+J,I)=A(I+J,I)+B(I,I+J)*G1(K)/2.D0
      I1=I+1
      I2=I+2
      I3=I+3
      A(I2,I1)=A(I2,I1)+B(I2,I1)*11.D0*F2(K)/50.D0
      A(I3,I1)=A(I3,I1)+B(I3,I1)*11.D0*F2(K)/50.D0
      A(I3,I2)=A(I3,I2)+B(I3,I2)*11.D0*F2(K)/50.D0
100   CONTINUE
110   CONTINUE
      DO 120 I=1,N
      KK=U(I)
120   ENERGY=ENERGY+.5D0*B(I,I)*(A(I,I)+Q(I))+.5D0*PSB(I,I)*(PS(I,I)+PSQ
     1(I))
      DO 130 I=1,NM
      II=U(I)
      LL=I+1
      DO 130 J=LL,N
      JJ=U(J)
130   ENERGY=ENERGY+B(I,J)*(A(I,J)+A(J,I))+PSB(I,J)*(PS(I,J)+PS(J,I))
```

```
      WRITE (6,240) ENERGY                                              SCFC 970
      IF (DABS(ENERGY-OLDENG).GE.1.00D-6) GO TO 140                     SCFC 980
      Z=100                                                             SCFC 990
      WRITE (6,250)                                                     SCFC1000
      GO TO 150                                                         SCFC1010
  140 CONTINUE                                                          SCFC1020
      OLDENG=ENERGY                                                     SCFC1030
  150 CONTINUE                                                          SCFC1040
      IF (Z.LE.IT) GO TO 170                                            SCFC1050
C     SYMMETRIZE F FOR PRINTING (MATRIX A)                              SCFC1060
      DO 160 I=1,N                                                      SCFC1070
      DO 160 J=I,N                                                      SCFC1080
  160 A(I,J)=A(J,I)                                                     SCFC1090
      WRITE (6,260)                                                     SCFC1100
      CALL SCFOUT (0,1)                                                 SCFC1110
      WRITE (6,270)                                                     SCFC1120
      CALL SCFOUT (0,3)                                                 SCFC1130
  170 CONTINUE                                                          SCFC1140
      CALL EIGN (N,RHO)                                                 SCFC1150
      IF (Z.LT.IT) GO TO 180                                            SCFC1160
      WRITE (6,280)                                                     SCFC1170
      CALL SCFOUT (1,2)                                                 SCFC1180
  180 DO 190 I=1,N                                                      SCFC1190
      DO 190 J=1,N                                                      SCFC1200
      HELP1(I,J)=A(I,J)                                                 SCFC1210
      HELP2(I,J)=B(I,J)                                                 SCFC1220
  190 A(I,J)=PS(I,J)                                                    SCFC1230
      CALL EIGN (N,RHO)                                                 SCFC1240
      DO 200 I=1,N                                                      SCFC1250
      DO 200 J=1,N                                                      SCFC1260
      PS(I,J)=A(I,J)                                                    SCFC1270
      PSB(I,J)=B(I,J)                                                   SCFC1280
```

```
      A(I,J)=HELP1(I,J)                                                 SCFC1290
200   B(I,J)=HELP2(I,J)                                                 SCFC1300
      IF (Z.LE.IT) GO TO 210                                            SCFC1310
      WRITE (6,290)                                                     SCFC1320
      CALL SCFOUT (1,4)                                                 SCFC1330
210   CONTINUE                                                          SCFC1340
C     EIGENVECTORS ( IN B ) ARE CONVERTED INTO DENSITY MATRIX (IN B)    SCFC1350
      CALL DEN (OCCA,2,N)                                               SCFC1360
      CALL DEN (1,4,N)                                                  SCFC1370
      DO 220 I=1,N                                                      SCFC1380
      DO 220 J=1,N                                                      SCFC1390
      PSB(I,J)=0.5D0*(PSB(I,J)+P(I,J))                                  SCFC1400
220   B(I,J)=0.5D0*(B(I,J)+S(I,J))                                      SCFC1410
      IF (Z.LE.IT) GO TO 50                                             SCFC1420
      RETURN                                                            SCFC1430
C                                                                       SCFC1440
230   FORMAT (1X,69H INITIAL POSITRON DENSITY MATRIX AND EIGENVALUES CALSCFC1450
     1CULATED FROM F(+)/)                                               SCFC1460
240   FORMAT (//,10X,21H ELECTRONIC ENERGY   ,F16.10)                   SCFC1470
250   FORMAT (5X,18H ENERGY SATISFIED /)                                SCFC1480
260   FORMAT (1X,36H ELECTRON HARTREE-FOCK ENERGY MATRIX/)              SCFC1490
270   FORMAT (1X,36H POSITRON HARTREE-FOCK ENERGY MATRIX/)              SCFC1500
280   FORMAT (1X,33H ELECTRON EIGENVALUES AND VECTORS/)                 SCFC1510
290   FORMAT (1X,33H POSITRON EIGENVALUES AND VECTORS/)                 SCFC1520
      END                                                               SCFC1530
```

```
      SUBROUTINE CPRINT
      IMPLICIT REAL*8(A-H,O-Z)
C      CNDO-INDO SCF CLOSED SHELL - PRINTOUT
      COMMON /ARRAYS/ A(80,80),B(80,80),D(80,80),PSB(80,80)
      COMMON /GAB/ XXX(400),G(35,35),Q(80),YYY(80),ENERGY,XXY(214)
      COMMON /INFO/ NATOMS,CHARGE,MULTIP,AN(35),C(35,3),N
      COMMON /INFO1/ CZ(35),U(80),ULIM(35),LLIM(35),NELECS,OCCA,OCCB
      COMMON /PERTBL/ EL(18)
      COMMON /OPTICM/ OPTION,OPNCLO,HUCKEL,CNDC,INDC,CLOSED,OPEN
      COMMON /ORB1/ ORB(9)
      INTEGER OPTION,OPNCLO,HUCKEL,CNDO,INDO,CLOSED,OPEN
      INTEGER CHARGE,OCCA,OCCB,UL,ULIM,U,AN,CZ,Z,EL,ANI,ORB
      INTEGER ULI,ULJ
      DIMENSION DPM(3), DM(3), DMSP(3), DMPD(3)
      DIMENSION ATENG(18)
      IF (OPTION.EQ.CNDO) GO TO 10
      ATENG(1)=-0.6387302462D0
      ATENG(3)=-.2321972405D0
      ATENG(4)=-1.1219620354D0
      ATENG(5)=-2.8725750048D0
      ATENG(6)=-5.9349548261D0
      ATENG(7)=-10.6731741251D0
      ATENG(8)=-17.2920850650D0
      ATENG(9)=-26.2574377875D0
      GO TO 20
10    CONTINUE
      ATENG(1)=-0.6387302462D0
      ATENG(3)=-.2321972405D0
      ATENG(4)=-1.1454120355D0
      ATENG(5)=-2.9774239048D0
      ATENG(6)=-6.1649936261D0
      ATENG(7)=-11.0768746252D0
```

```
      ATENG(8)=-18.0819658651D0
      ATENG(9)=-27.5491302880D0
      ATENG(11)=-.1977009568D0
      ATENG(12)=-.8671913833D0
      ATENG(13)=-2.0364557744D0
      ATENG(14)=-3.8979034686D0
      ATENG(15)=-6.7966009163D0
      ATENG(16)=-10.7658174341D0
      ATENG(17)=-16.0467017940D0
20    CONTINUE
      K=NATOMS-1
      WRITE (6,160)
      CALL SCFOUT (0,2)
      WRITE (6,170)
      CALL SCFOUT (0,4)
      IF (NATOMS.EQ.1) GO TO 40
      DO 30 I=1,K
      L=I+1
      DO 30 J=L,NATOMS
      RAD=DSQRT((C(I,1)-C(J,1))**2+(C(I,2)-C(J,2))**2+(C(I,3)-C(J,3))**2
     1)
30    ENERGY=ENERGY+(DFLOAT(CZ(I))*DFLOAT(CZ(J)))/RAD
40    WRITE (6,180) ENERGY
      DO 50 I=1,NATOMS
      ANI=AN(I)
50    ENERGY=ENERGY-ATENG(ANI)
      WRITE (6,190) ENERGY
      WRITE (6,200)
      DO 70 I=1,NATOMS
      TCHG=0.D0
      PSCH=0.0D0
      LL=LLIM(I)
```

```
      UL=ULIM(I)
      DO 60 J=LL,UL
      PSCH=PSCH+PSB(J,J)
60    TCHG=TCHG+B(J,J)
      ANI=AN(I)
      WRITE (6,210) I,EL(ANI),TCHG,PSCH
      XXX(I)=TCHG
70    CONTINUE
      DO 80 I=1,3
      DM(I)=0.0D0
      DMSP(I)=0.D0
80    DMPD(I)=0.D0
      DO 140 J=1,NATOMS
      IF (AN(J).LT.3) GO TO 120
      IF (AN(J).LT.11) GO TO 100
      SLTR1=(.65D0*DFLOAT(AN(J))-4.95D0)/3.D0
      FACTOR=2.5416D0*7.D0/(DSQRT(5.D0)*SLTR1)
      INDEX=LLIM(J)
      DO 90 K=1,3
90    DMSP(K)=DMSP(K)-B(INDEX,INDEX+K)*10.27175D0/SLTR1
      DMPD(1)=DMPD(1)-FACTOR*(B(INDEX+2,INDEX+8)+B(INDEX+3,INDEX+5)+B(IN
     1DEX+1,INDEX+7)-1.D0/DSQRT(3.D0)*B(INDEX+1,INDEX+4))
      DMPD(2)=DMPD(2)-FACTOR*(B(INDEX+1,INDEX+8)+B(INDEX+3,INDEX+6)+B(IN
     1DEX+2,INDEX+7)-1.D0/DSQRT(3.D0)*B(INDEX+2,INDEX+4))
      DMPD(3)=DMPD(3)-FACTOR*(B(INDEX+1,INDEX+5)+B(INDEX+2,INDEX+6)+2.D0
     1/DSQRT(3.D0)*B(INDEX+3,INDEX+4))
      GO TO 120
100   INDEX=LLIM(J)
      DO 110 K=1,3
110   DMSP(K)=DMSP(K)-B(INDEX,INDEX+K)*7.33697D0/(.325D0*DFLOAT(AN(J)-1)
     1)
120   DO 130 I=1,3
```

```
130   DM(I)=DM(I)+(DFLOAT(CZ(J))-XXX(J))*C(J,I)*2.5416D0                CPRT 970
140   CONTINUE                                                          CPRT 980
      DO 150 I=1,3                                                      CPRT 990
150   DPM(I)=DM(I)+DMSP(I)+DMPD(I)                                      CPRT1000
      WRITE (6,220)                                                     CPRT1010
      WRITE (6,230)                                                     CPRT1020
      WRITE (6,240) DM(1),DM(2),DM(3)                                   CPRT1030
      WRITE (6,250) DMSP(1),DMSP(2),DMSP(3)                             CPRT1040
      WRITE (6,260) DMPD(1),DMPD(2),DMPD(3)                             CPRT1050
      WRITE (6,270) DPM(1),DPM(2),DPM(3)                                CPRT1060
      DP=DSQRT(DPM(1)**2+DPM(2)**2+DPM(3)**2)                           CPRT1070
      WRITE (6,280) DP                                                  CPRT1080
      RETURN                                                            CPRT1090
C                                                                       CPRT1100
160   FORMAT (1X,24H ELECTRON DENSITY MATRIX/)                          CPRT1110
170   FORMAT (1X,24H POSITRON DENSITY MATRIX/)                          CPRT1120
180   FORMAT (//,10X,16H TOTAL ENERGY = ,F16.10)                        CPRT1130
190   FORMAT (//,10X,16HBINDING ENERGY= ,F16.10,5H A.U./)               CPRT1140
200   FORMAT (10X,32H(-)CHG DENSITY    (+)CHG DENSITY)                  CPRT1150
210   FORMAT (I3,A4,8X,F7.4,11X,F7.4)                                   CPRT1160
220   FORMAT (//,20X,16H  DIPOLE MOMENTS,/)                             CPRT1170
230   FORMAT (5X,11H COMPONENTS,3X,2H X,8X,2H Y,8X,2H Z)                CPRT1180
240   FORMAT (5X,10H DENSITIES,3(1X,F9.5))                              CPRT1190
250   FORMAT (5X,4H S,P,6X,3(1X,F9.5))                                  CPRT1200
260   FORMAT (5X,4H P,D,6X,3(1X,F9.5))                                  CPRT1210
270   FORMAT (5X,6H TOTAL,4X,3(1X,F9.5),/)                              CPRT1220
280   FORMAT (3X,15H DIPOLE MOMENT=,F9.5,7H DEBYES,//)                  CPRT1230
      END                                                               CPRT1240
```

```
C     PROGRAM PAL
C     A PROGRAM FOR THE ANALYSIS OF DECAY CURVES
C     VERSION FOR IBM 360
C     INCLUDING AN ITERATIVE PROCEDURE FOR DETERMINATION OF HALF LIVES
C     WITH REVISED RJT ROUTINE. - CAUSES OLD ROUTINE TO BE USED.
C     USING DOUBLE PRECISION INVERSION ROUTINE BNSINV
      DOUBLE PRECISION B(10,10)
      DOUBLE PRECISION U(10,10),BR(10,10)
      DOUBLE PRECISION T(512),F(512),SFSQ(512),H(10),D(10),A(512,10),APF
     1(10),FCALC(512),SF(200),SIGMAH(10),X(10),SIGMAD(10),DELTAD(10,9),D
     2DELTA(10,9),XPDTO(10),XEOB(10),SXEOB(10),UNITK(10),TAU(10),ANN(10)
      DOUBLE PRECISION BADT(512),BADFS(512),BINVRS(10,10),FKCS(5),SFKCS(
     15),RATIO(512),V(512)
      DOUBLE PRECISION DT,DABS,DSQRT,DEXP
      EQUIVALENCE (BADT,SF), (BADFS,V), (BINVRS,B)
      DIMENSION AA(5), SLOP(5), YCAL(512)
      DIMENSION CCMNT(8), NAME(11), JUNIT(10)
      INTEGER HR,DAY,YR
      INTEGER CMIT
      DATA HR,DAY,YR/1HH,1HD,1HY/
      READ (5,890) COMNT
C     ENTRANCE TO PROGRAM
C     INPUT
      AIM=0.0
20    LT1=0
      READ (5,890) IDENT,NAME,IENDS
      IF (IENDS.EQ.0) GO TO 40
      IF (AIM.EQ.0.0) GO TO 30
      CALL PLOT (0.0,0.0,-4)
30    CALL EXIT
C     NC IS NO. OF COMPONENTS
C     NV IS NO. OF UNKNOWN HALF LIVES
```

```
C      NCNV ALWAYS EQUALS ONE
C      CNV GOVERNS HOW FAR ITERATIONS WILL PROCEED; IF CNV IS ZERO A
C               MAX. OF NINE ITERATIONS WILL BE PERFORMED
C      BGD IS THE COUNTER BACKGROUND FOR SUBTRACTION
C      SBGD IS THE STANDARD DEVIATION FOR ROOT-MEAN-SQUARE ADDITION TO
C      THE STANDARD DEVIATION OF EACH POINT (USUALLY ZERO)
C      IN... INPUT CONTROL (ZERO OR BLANK CAUSES USE OF PROGRAM INPUT
C           FORMAT; POSITIVE INTEGER TRANSFERS TO SUBROUTINE INPUT)
C      IT...NUMBER HERE CAUSES INTERMEDIATE MATRICES TO BE PRINTED
C                    (USUALLY LEFT BLANK)
C      BLOCK IS THE COUNTER DEAD TIME (USUALLY LEFT BLANK)
C      SCOFF IS CUTOFF (IN PERCENT) ON THE SMALLEST VALUE AT WHICH THE
C      PROGRAM WILL USE THE STANDARD DEVN. FROM STATS. ALONE (0.5)
C      RJT...IF NOT BLANK OR ZERO PROGRAM EXAMINES ITS OUTPUT AND
C      REJECTS POINTS WHICH FALL FURTHER THAN RJT TIMES THE STANDARD
C      DEVN. FROM THE CURVE. THE FIT IS THEN REPEATED
C      KCS...CAUSES THE PROGRAM TO ENTER A KNOWN COMPT. SUBTRACTION
C           ROUTINE (USUALLY SET AT ZERO)
C      ICARD IF UNEQUAL TO ZERO CAUSES PROGRAM TO ENTER INTENSITY
C           ROUTINE (USUALLY EQUALS ZERO)
C      INP...IF EQUAL TO ZERO OR BLANK ALLOWS HALF-LIFE GUESSES TO BE
C      ENTERED AS HALF-LIVES AFTER TIME-PER-CHANNEL CORRECTION; IF
C      EQUAL TO ONE ALLOWS TAU GUESSES TO BE USED
C      OMIT...DATA OUTPUT OPTIONS
C                     OMIT=1:OUTPUT INCLUDES ALL DATA, INCLUDES GRAPH
C                     OMIT=2:OMITS SUPERFLUOUS DATA, INCLUDES GRAPH
C                     OMIT=3:INCLUDES ALL DATA, OMITS GRAPH
C                     OMIT=4: OMITS SUPERFLUOUS DATA, OMITS GRAPH
40     READ (5,900) NC,NV,NCNV,CNV,BGD,SBGD,IN,IT,BLOCK,SCOFF,RJT,KCS,ICA
      1RD,INP,OMIT
       IF (OMIT) 50,50,60
50     WRITE (6,910)
```

```
      GO TO 30
   60 IF (OMIT-5) 70,50,50
   70 IF (INP.EQ.0) GO TO 90
      READ (5,920) CALIB
      DO 80 I=1,NC
      READ (5,920) TAU(I),JUNIT(I)
      H(I)=(TAU(I)*0.69314718)/CALIB
   80 D(I)=0.69314718/H(I)
      GO TO 110
   90 DO 100 I=1,NC
      READ (5,920) H(I),JUNIT(I)
C     HALF LIFE INPUT CONVERSION.  H,D, OR Y ARE RECOGNIZED AS SUCH.
C     OTHER CHARACTERS ARE TAKEN TO MEAN M.
      UNITK(I)=0.69314718D0
      IF (JUNIT(I).EQ.HR) UNITK(I)=0.11552453D-1
      IF (JUNIT(I).EQ.DAY) UNITK(I)=0.48135221D-3
      IF (JUNIT(I).EQ.YR) UNITK(I)=0.13178987D-5
      D(I)=UNITK(I)/H(I)
  100 CONTINUE
  110 NP=0
      NSCHAN=0
C     INPUT OPTION
      IF (IN.EQ.0) GO TO 120
      CALL INPUT (T,F,SFSQ,NP,BGD,NSCHAN)
      GO TO 130
  120 NP=NP+1
      READ (5,930) T(NP),F(NP),SFSQ(NP)
      IF (SFSQ(NP).NE.0.) GO TO 120
C     TIME NORMALIZATION
  130 DO 140 I=2,NP
      T(I)=T(I)-T(1)
  140 CONTINUE
```

```
      T(1)=0.0D0
      TO=T(NP)
      NP=NP-1
      NP1=NP
      NC1=NC
      IF (BLOCK.EQ.0.) GO TO 160
C     DEAD TIME CORRECTION
      DEADT=BLOCK*(1.67E-8)
      DO 150 I=1,NP
  150 F(I)=F(I)/(1.-DEADT*F(I))
  160 IF (BGD.LE.0.) GO TO 180
      SBGDSQ=SBGD**2
      DO 170 I=1,NP
      F(I)=F(I)-BGD
  170 SFSQ(I)=SFSQ(I)+SBGDSQ
C     SUBROUTINE FOR SIGMA CUTOFF
  180 IF (SCOFF.EQ.0.) GO TO 200
      SCOFSQ=SCOFF**2/10000.
      DO 190 I=1,NP
      TSFSQ=SCOFSQ*F(I)**2
      IF (SFSQ(I).LT.TSFSQ) SFSQ(I)=TSFSQ
  190 CONTINUE
C     KNOWN COMPONENT SUBTRACTION (KCS) ROUTINE
  200 IF (KCS.EQ.0) GO TO 240
      READ (5,940) (FKCS(I),SFKCS(I),I=1,KCS)
      DO 230 J=1,KCS
      ND=NC-KCS+J
      DO 210 I=1,NP
      FACTOR=DEXP((TO-T(I))*D(ND))
      IF ((F(I)-(FKCS(J)*FACTOR)).LE.0.0D0) GO TO 220
      F(I)=F(I)-FKCS(J)*FACTOR
      SFSQ(I)=SFSQ(I)+(SFKCS(J)*FACTOR)**2
```

```
  210 CONTINUE                                                          PAL 1290
  220 NP=NP-1                                                           PAL 1300
  230 CONTINUE                                                          PAL 1310
      NC=NC-KCS                                                         PAL 1320
C     INITIALIZATION AND RETURNS                                        PAL 1330
  240 NITER=-1                                                          PAL 1340
      IF (NV.EQ.0) GO TO 250                                            PAL 1350
      LT1=1                                                             PAL 1360
      NVTEMP=NV                                                         PAL 1370
      NV=0                                                              PAL 1380
C     RETURN AFTER FIXED HALF LIFE PASS                                 PAL 1390
  250 NT=NC+NV                                                          PAL 1400
      LV=NC+1                                                           PAL 1410
C     CALCULATION OF A MATRIX                                           PAL 1420
C                ALSO RETURN FOR NEXT ITERATION                         PAL 1430
  260 NITER=NITER+1                                                     PAL 1440
      DO 300 I=1,NP                                                     PAL 1450
      DO 280 J=1,NC                                                     PAL 1460
      DT=-D(J)*T(I)                                                     PAL 1470
      IF ((DT).GT.(-34.5D0)) GO TO 270                                  PAL 1480
      A(I,J)=0.0D0                                                      PAL 1490
      GO TO 280                                                         PAL 1500
  270 A(I,J)=DEXP(DT)                                                   PAL 1510
  280 CONTINUE                                                          PAL 1520
      IF (NV.LE.0) GO TO 300                                            PAL 1530
      DO 290 J=LV,NT                                                    PAL 1540
      K=J-NC                                                            PAL 1550
  290 A(I,J)=T(I)*A(I,K)                                                PAL 1560
  300 CONTINUE                                                          PAL 1570
      IF (IT) 310,320,310                                               PAL 1580
  310 WRITE (6,950) ((A(I,J),J=1,NT),I=1,2)                             PAL 1590
C     CONSTRUCT MATRIX APF                                              PAL 1600
```

```
C                    ALSO RETURN AFTER DATA REJECTION                   PAL 1610
320   DO 330 I=1,NT                                                     PAL 1620
      APF(I)=0.0D0                                                      PAL 1630
      DO 330 K=1,NP                                                     PAL 1640
      APF(I)=APF(I)+A(K,I)*F(K)/SFSQ(K)                                 PAL 1650
330   CONTINUE                                                          PAL 1660
      IF (IT) 340,350,340                                               PAL 1670
340   WRITE (6,950) (APF(I),I=1,NT)                                     PAL 1680
C     CONSTRUCT MATRIX B                                                PAL 1690
350   DO 360 I=1,NT                                                     PAL 1700
      DO 360 J=1,NT                                                     PAL 1710
      B(I,J)=0.0D0                                                      PAL 1720
      DO 360 K=1,NP                                                     PAL 1730
      B(I,J)=B(I,J)+A(K,I)*A(K,J)/SFSQ(K)                               PAL 1740
360   CONTINUE                                                          PAL 1750
      IF (IT) 370,390,370                                               PAL 1760
370   WRITE (6,950) ((B(I,J),J=1,NT),I=1,NT)                            PAL 1770
      DO 380 KI=1,NT                                                    PAL 1780
      DO 380 KJ=1,NT                                                    PAL 1790
380   BR(KI,KJ)=B(KI,KJ)                                                PAL 1800
C     B MATRIX INVERSION                                                PAL 1810
390   EPSIL=0.0D0                                                       PAL 1820
      CALL BNSINV (B,NT,DETERM,EPSIL,ITEST)                             PAL 1830
C     B MATRIX IS NOW REPLACED BY ITS INVERSE, BINVRS.                  PAL 1840
      IF (ITEST.NE.0) GO TO 580                                         PAL 1850
      IF (IT) 400,420,400                                               PAL 1860
400   WRITE (6,950) ((BINVRS(I,J),J=1,NT),I=1,NT)                       PAL 1870
      DO 410 I=1,NT                                                     PAL 1880
      DO 410 J=1,NT                                                     PAL 1890
      U(I,J)=0.0D0                                                      PAL 1900
      DO 410 K=1,NT                                                     PAL 1910
410   U(I,J)=U(I,J)+BINVRS(I,K)*BR(K,J)                                 PAL 1920
```

```
      WRITE (6,950) ((U(I,J),J=1,NT),I=1,NT)                             PAL 1930
C     SOLUTION OF NORMAL EQUATIONS                                       PAL 1940
420   DO 430 I=1,NT                                                      PAL 1950
      X(I)=0.0D0                                                         PAL 1960
      DO 430 J=1,NT                                                      PAL 1970
      X(I)=X(I)+BINVRS(I,J)*APF(J)                                       PAL 1980
430   CONTINUE                                                           PAL 1990
C     ENTRANCE TO CALCULATIONS FOR OUTPUT(127) OR ITERATION TESTS(301)   PAL 2000
      IF (NV.NE.0) GO TO 500                                             PAL 2010
C     CALCULATIONS FOR OUTPUT DATA                                       PAL 2020
440   DO 450 I=1,NC                                                      PAL 2030
      SIGMAH(I)=0.0D0                                                    PAL 2040
450   XPDTO(I)=DEXP(-TO*D(I))                                            PAL 2050
C     HALF LIFE OUTPUT CONVERSION                                        PAL 2060
      IF (NV.EQ.0) GO TO 580                                             PAL 2070
      IF (INP.EQ.0) GO TO 470                                            PAL 2080
      DO 460 I=1,NV                                                      PAL 2090
      H(I)=0.69314718/D(I)                                               PAL 2100
460   SIGMAH(I)=H(I)*SIGMAD(I)/D(I)                                      PAL 2110
      GO TO 490                                                          PAL 2120
470   DO 480 I=1,NV                                                      PAL 2130
      H(I)=UNITK(I)/D(I)                                                 PAL 2140
480   SIGMAH(I)=H(I)*SIGMAD(I)/D(I)                                      PAL 2150
490   GO TO 580                                                          PAL 2160
C     TESTS FOR COMPLETION OF ITERATION                                  PAL 2170
500   NON=1                                                              PAL 2180
      DO 520 I=1,NV                                                      PAL 2190
      L=I+NC                                                             PAL 2200
      DELTAD(I,NITER)=-X(L)/X(I)                                         PAL 2210
      DDELTA(I,NITER)=DABS(DELTAD(I,NITER))                              PAL 2220
510   IF (DABS(DELTAD(I,NITER)).LT.0.5D0*DABS(D(I))) GO TO 520           PAL 2230
C     CHANGE IN THE DECAY CONSTANT CANNOT EXCEED HALF ITS VALUE          PAL 2240
```

```
      DELTAD(I,NITER)=0.75D0*DELTAD(I,NITER)                            PAL 2250
      GO TO 510                                                         PAL 2260
  520 D(I)=D(I)+DELTAD(I,NITER)                                         PAL 2270
      IF (NITER.LE.2) GO TO 260                                         PAL 2280
      IF (NCNV.GT.0) GO TO 540                                          PAL 2290
      DO 530 I=1,NV                                                     PAL 2300
      IF (DDELTA(I,NITER).LE.DDELTA(I,NITER-1)) GO TO 530               PAL 2310
      IF (DDELTA(I,NITER-1).GT.DDELTA(I,NITER-2)) GO TO 550             PAL 2320
  530 CONTINUE                                                          PAL 2330
  540 NON=0                                                             PAL 2340
  550 DO 560 I=1,NV                                                     PAL 2350
      L=I+NC                                                            PAL 2360
  560 SIGMAD(I)=DSQRT(BINVRS(L,L))/DABS(X(I))                           PAL 2370
      IF (NON.EQ.1) GO TO 440                                           PAL 2380
      IF (NITER.GE.9) GO TO 440                                         PAL 2390
      DO 570 I=1,NV                                                     PAL 2400
      IF (DABS(DELTAD(I,NITER)).GE.CNV*SIGMAD(I)) GO TO 260             PAL 2410
  570 CONTINUE                                                          PAL 2420
      GO TO 440                                                         PAL 2430
C     PRINT OUT RESULTS                                                 PAL 2440
  580 WRITE (6,960) COMNT                                               PAL 2450
      WRITE (6,970) IDENT,NAME                                          PAL 2460
      IF (ITEST.EQ.0) GO TO 590                                         PAL 2470
      WRITE (6,980)                                                     PAL 2480
      GO TO 20                                                          PAL 2490
  590 WRITE (6,990) NP,NC,NV,CNV,BGD,SBGD,BLOCK,SCOFF,RJT,KCS           PAL 2500
      IF (NV.EQ.0) GO TO 630                                            PAL 2510
      IF (NON.EQ.1) GO TO 600                                           PAL 2520
      WRITE (6,1000) NITER                                              PAL 2530
      GO TO 610                                                         PAL 2540
  600 WRITE (6,1010) NITER                                              PAL 2550
  610 WRITE (6,1020)                                                    PAL 2560
```

```
      WRITE (6,1030) (D(I),I=1,NV)                                      PAL 2570
      DO 620 J=1,NITER                                                  PAL 2580
      WRITE (6,1040) J,(DELTAD(I,J),I=1,NV)                             PAL 2590
620   CONTINUE                                                          PAL 2600
      WRITE (6,1050) (SIGMAD(I),I=1,NV)                                 PAL 2610
C     CONVERSION TO EOB                                                 PAL 2620
630   DO 640 I=1,NC                                                     PAL 2630
      XEOB(I)=X(I)*XPDTO(I)                                             PAL 2640
      SXEOB(I)=BINVRS(I,I)                                              PAL 2650
      IF (I.GT.NV) GO TO 640                                            PAL 2660
      L=I+NC                                                            PAL 2670
      SXEOB(I)=SXEOB(I)+2.*TO*BINVRS(I,L)+TO**2*BINVRS(L,L)             PAL 2680
640   SXEOB(I)=XPDTO(I)*DSQRT(DABS(SXEOB(I)))                           PAL 2690
      DO 650 I=1,NC                                                     PAL 2700
650   TAU(I)=(H(I)*CALIB)/0.69314718                                    PAL 2710
      WRITE (6,1060)                                                    PAL 2720
      WRITE (6,1070) (I,H(I),JUNIT(I),SIGMAH(I),JUNIT(I),XEOB(I),SXEOB(IPAL 2730
     1),XPDTO(I),TAU(I),I=1,NC)                                         PAL 2740
      IF (KCS.EQ.0) GO TO 670                                           PAL 2750
      I=NC                                                              PAL 2760
      J=0                                                               PAL 2770
660   I=I+1                                                             PAL 2780
      J=J+1                                                             PAL 2790
      WRITE (6,1080) I,H(I),JUNIT(I),FKCS(J),SFKCS(J)                   PAL 2800
      IF (KCS.GT.J) GO TO 660                                           PAL 2810
670   VPV=0.0                                                           PAL 2820
      DO 690 I=1,NP                                                     PAL 2830
      FCALC(I)=0.0D0                                                    PAL 2840
      DO 680 J=1,NC                                                     PAL 2850
      FCALC(I)=FCALC(I)+A(I,J)*X(J)                                     PAL 2860
680   CONTINUE                                                          PAL 2870
      V(I)=F(I)-FCALC(I)                                                PAL 2880
```

```
      SF(I)=DSQRT(SFSQ(I))                                              PAL 2890
      RATIO(I)=V(I)/SF(I)                                               PAL 2900
      VPV=VPV+V(I)**2/SFSQ(I)                                           PAL 2910
  690 CONTINUE                                                          PAL 2920
      DF=NP-NT                                                          PAL 2930
      FIT=SQRT(VPV/DF)                                                  PAL 2940
      WRITE (6,1090) FIT                                                PAL 2950
      GO TO (700,710,700,710), OMIT                                     PAL 2960
  700 WRITE (6,1100)                                                    PAL 2970
      WRITE (6,1110) (T(I),F(I),FCALC(I),V(I),SF(I),RATIO(I),I=1,NP)    PAL 2980
  710 IF (RJT.EQ.0.) GO TO 800                                          PAL 2990
      IF (NV.NE.0) GO TO 800                                            PAL 3000
C     DATA REJECTION SUBROUTINE                                         PAL 3010
      I=0                                                               PAL 3020
      NRJT=0                                                            PAL 3030
  720 I=I+1                                                             PAL 3040
  730 IF (I.GT.NP) GO TO 780                                            PAL 3050
      IF (DABS(RATIO(I)).LE.ABS(RJT)) GO TO 720                         PAL 3060
      IF (RJT.LT.0.) GO TO 760                                          PAL 3070
      IF (I.EQ.NP) GO TO 750                                            PAL 3080
      IF (RATIO(I)*RATIO(I+1)) 740,740,720                              PAL 3090
  740 IF (I.EQ.1) GO TO 760                                             PAL 3100
  750 IF (RATIO(I)*RATIO(I-1)) 760,760,720                              PAL 3110
  760 NRJT=NRJT+1                                                       PAL 3120
      BADT(NRJT)=T(I)                                                   PAL 3130
      BADFS(NRJT)=F(I)                                                  PAL 3140
      NP=NP-1                                                           PAL 3150
C     MOVE UP REMAINING POINTS                                          PAL 3160
      DO 770 J=I,NP                                                     PAL 3170
      T(J)=T(J+1)                                                       PAL 3180
      F(J)=F(J+1)                                                       PAL 3190
      SFSQ(J)=SFSQ(J+1)                                                 PAL 3200
```

```
      RATIO(J)=RATIO(J+1)                                               PAL 3210
      DO 770 K=1,NT                                                     PAL 3220
      A(J,K)=A(J+1,K)                                                   PAL 3230
770   CONTINUE                                                          PAL 3240
      GO TO 730                                                         PAL 3250
780   IF (NRJT.NE.0) GO TO 790                                          PAL 3260
      WRITE (6,1120)                                                    PAL 3270
      GO TO 800                                                         PAL 3280
790   WRITE (6,1130) NRJT                                               PAL 3290
      WRITE (6,1140) (BADT(I),BADFS(I),I=1,NRJT)                        PAL 3300
      WRITE (6,1150)                                                    PAL 3310
      GO TO 320                                                         PAL 3320
800   IF (LT1.NE.1) GO TO 810                                           PAL 3330
      LT1=0                                                             PAL 3340
      NV=NVTEMP                                                         PAL 3350
      GO TO 250                                                         PAL 3360
810   GO TO (820,820,830,830), OMIT                                     PAL 3370
820   CALL POL (F,FCALC,NP,IDENT)                                       PAL 3380
      AIM=1.0                                                           PAL 3390
830   IF (ICARD.EQ.0) GO TO 20                                          PAL 3400
      T(1)=-TO                                                          PAL 3410
      STX=T(1)                                                          PAL 3420
      DO 840 L=2,NP1                                                    PAL 3430
      T(L)=T(L-1)+1.0D0                                                 PAL 3440
840   CONTINUE                                                          PAL 3450
      DO 850 K=1,NP1                                                    PAL 3460
      FCALC(K)=0.0D0                                                    PAL 3470
      DO 850 J=1,NC1                                                    PAL 3480
      FCALC(K)=FCALC(K)+XEOB(J)*DEXP(-D(J)*T(K))                        PAL 3490
850   CONTINUE                                                          PAL 3500
      DO 860 I=1,NP1                                                    PAL 3510
      YCAL(I)=FCALC(I)                                                  PAL 3520
```

```
860   CONTINUE                                                          PAL 3530
      DO 870 I=1,NC1                                                    PAL 3540
      AA(I)=XEOB(I)                                                     PAL 3550
      SLOP(I)=D(I)                                                      PAL 3560
870   CONTINUE                                                          PAL 3570
      CALL INTENS (IDENT,NAME,BGD,STX,NC,NP,AA,SLOP,YCAL,OMIT)          PAL 3580
C     CAL. OF ANNIHILATION RATES                                        PAL 3590
      DO 880 I=1,NC                                                     PAL 3600
      ANN(I)=1.0/TAU(I)                                                 PAL 3610
880   CONTINUE                                                          PAL 3620
      WRITE (6,1160) (TAU(I),I=1,NC)                                    PAL 3630
      WRITE (6,1170) (ANN(I),I=1,NC)                                    PAL 3640
      WRITE (6,1180) CALIB                                              PAL 3650
      WRITE (6,1190) FIT                                                PAL 3660
      GO TO 20                                                          PAL 3670
C                                                                       PAL 3680
890   FORMAT (A4,11A4,I2)                                               PAL 3690
900   FORMAT (2I3,I2,F6.4,2F8.2,2I2,3F5.2,4I2)                          PAL 3700
910   FORMAT (1H1,49H       PROGRAM FAILURE,OMIT ERROR: DATA CANCELLED) PAL 3710
920   FORMAT (F10.5,A1)                                                 PAL 3720
930   FORMAT (3E15.8)                                                   PAL 3730
940   FORMAT (F16.8,F14.8)                                              PAL 3740
950   FORMAT (/1H ,9E14.7)                                              PAL 3750
960   FORMAT (1H1,12A4)                                                 PAL 3760
970   FORMAT (1H0,A4,11A4)                                              PAL 3770
980   FORMAT (50HOMATRIX INVERSION HAS FAILED. MORE DATA IS NEEDED.)    PAL 3780
990   FORMAT (//4H NP=,I3,4H NC=,I2,4H NV=,I1,5H CNV=,F6.4,5H BGD=,F8.2,PAL 3790
     16H SBGD=,F8.2,7H BLOCK=,F5.2,7H SCOFF=,F5.2,5H RJT=,F6.4,5H KCS=,IPAL 3800
     22)                                                                PAL 3810
1000  FORMAT (//25H    ITERATIONS PERFORMED=,I2,15H     CONVERGENT)     PAL 3820
1010  FORMAT (//25H    ITERATIONS PERFORMED=,I2,15H  NONCONVERGENT)     PAL 3830
1020  FORMAT (//86H             1ST COMP        2ND COMP        3RD COMPAL 3840
```

```
     1P        4TH COMP        5TH COMP)                                PAL 3850
1030  FORMAT (10H    D     ,5E16.8)                                     PAL 3860
1040  FORMAT (7H DELTA(,I2,1H),5E16.8)                                  PAL 3870
1050  FORMAT (10H  SIGMA   ,5E16.8)                                     PAL 3880
1060  FORMAT (//99H              HALF LIFE   SIGMA H          CPM AT EOBPAL 3890
     1        SIGMA          DECAY FACTOR        TAU)                   PAL 3900
1070  FORMAT (6H COMP(,I2,2H) ,F13.8,A1,F13.8,A1,3E17.8,F15.8)          PAL 3910
1080  FORMAT (6H COMP(,I2,2H) ,F10.5,A1,9X,2E16.8,17H  KNOWN COMPONENT) PAL 3920
1090  FORMAT (//8H    FIT=,F10.5//)                                     PAL 3930
1100  FORMAT (98H        T(I)             F(I)           FCALC(I)       PAL 3940
     1    V(I)           SIGMAF(I)       RATIO(I))                      PAL 3950
1110  FORMAT (1H ,5E17.8,2X,F10.5)                                      PAL 3960
1120  FORMAT (20H0ALL DATA POINTS OK.)                                  PAL 3970
1130  FORMAT (22H0DATA POINTS REJECTED(,I3,18H) ARE GIVEN BELOW./28H    PAL 3980
     1  BAD T            BAD F)                                         PAL 3990
1140  FORMAT (1H ,2E16.8)                                               PAL 4000
1150  FORMAT (41H0REPEAT CALCULATION WITHOUT THESE POINTS.)             PAL 4010
1160  FORMAT (//5X,24HLIFETIME (TAU) X 10-9SEC,4X,5F16.8)               PAL 4020
1170  FORMAT (//5X,28HANNIHILATION RATE  X 10+9SEC,5F16.8)              PAL 4030
1180  FORMAT (//37H    CALIBRATION (10-9SEC PER CHAN.) =,F10.5)         PAL 4040
1190  FORMAT (//16H            FIT=,F10.5)                              PAL 4050
      END                                                               PAL 4060
      SUBROUTINE INPUT (T,F,SFSQ,NP,BGD,NSCHAN)                         INPT  10
C     INPUT REVISED FOR POSITRON LIFETIME DATA  4/30/70                 INPT  20
C     NZCHAN EQUALS ZERO CHANNEL NUMBER                                 INPT  30
C     NSCHAN EQUALS STARTING CHANNEL NO. FOR DATA USED IN CALC LIFETIME INPT  40
C     NP EQUALS NO. OF DATA POINTS USED IN CALC TAU                     INPT  50
      DOUBLE PRECISION T(512),F(512),SFSQ(512)                          INPT  60
      READ (5,50) NZCHAN,NSCHAN,NP,CONTR                                INPT  70
      IF (CONTR.NE.0) GO TO 10                                          INPT  80
      READ (5,60) (F(I),I=1,NP)                                         INPT  90
      GO TO 20                                                          INPT 100
```

```
10    READ (5,70) (F(I),I=1,NP)
20    DO 30 I=1,NP
30    SFSQ(I)=F(I)
      NP=NP+1
      DO 40 I=1,NP
40    T(I)=NSCHAN-1+I
      T(NP)=NZCHAN
      RETURN
C
50    FORMAT (4I5)
60    FORMAT (F6.0,9F7.0)
70    FORMAT (F9.0,7F10.0)
      END
      SUBROUTINE BNSINV (A,N,DETERM,EPSIL,ITEST)
C     MATRIX INVERSION SUBROUTINE
C     CALLING SEQUENCE  CALLBNSINV(A,N,DETERM,EPSIL,ITEST)
C     A IS ORIGINAL MATRIX (REPLACED BY A-INVERSE AT END OF PROGRAM)
C     EL IS A 10 BY 10 ARRAY USED ONLY FOR WORKING STORAGE
C     N  IS DIMENSION OF MATRIX
C     DETERM IS LOCATION OF DETERMINANT
C     EPSIL IS USED TO TEST WHETHER MATRIX IS SINGULAR.
C           IF,AFTER TRIANGULARIZING THE MATRIX, THE RATIO OF THE
C           SMALLEST TO LARGEST DIAGONAL ELEMENT IS LESS THEN EPSIL
C           THE MATRIX IS CONSIDERED SINGULAR. IF ONE SETS EPSIL=0.
C           THE ROUTINE WILL USE EPSIL=1.D-10
C     ITEST IS AN ERROR INDICATOR.
C           IF ITEST = 0  ALL WENT WELL
C           IF ITEST = 1  MATRIX WAS FOUND TO BE SINGULAR
C           IF ITEST =-1  DIVIDE CHECK OCCURRED
      DOUBLE PRECISION A(10,10),EL(10,10),DABS,DSQRT
      DOUBLE PRECISION D,S,C,DETERM,DETERP,EPSIL,EPSILP
      DOUBLE PRECISION E
```

```
      IF (N.GT.1) GO TO 10                                              BNSI 200
C     SPECIAL CASE FOR N=1                                              BNSI 210
      A(1,1)=1.0D0/A(1,1)                                               BNSI 220
      GO TO 170                                                         BNSI 230
C     SET EL = IDENTITY MATRIX                                          BNSI 240
10    DO 20 J=1,N                                                       BNSI 250
      DO 20 I=1,N                                                       BNSI 260
      IF (I.EQ.J) EL(I,J)=1.0D0                                         BNSI 270
      IF (I.NE.J) EL(I,J)=0.0D0                                         BNSI 280
20    CONTINUE                                                          BNSI 290
C     TRIANGULARIZE A, FORM EL                                          BNSI 300
      N1=N-1                                                            BNSI 310
      M=2                                                               BNSI 320
      DO 60 J=1,N1                                                      BNSI 330
      DO 50 I=M,N                                                       BNSI 340
      IF (A(I,J).EQ.0.) GO TO 50                                        BNSI 350
      D=DSQRT(A(J,J)**2+A(I,J)**2)                                      BNSI 360
      C=A(J,J)/D                                                        BNSI 370
      S=A(I,J)/D                                                        BNSI 380
      DO 30 K=J,N                                                       BNSI 390
      D=C*A(J,K)+S*A(I,K)                                               BNSI 400
      A(I,K)=C*A(I,K)-S*A(J,K)                                          BNSI 410
      A(J,K)=D                                                          BNSI 420
30    CONTINUE                                                          BNSI 430
      DO 40 K=1,N                                                       BNSI 440
      D=C*EL(J,K)+S*EL(I,K)                                             BNSI 450
      EL(I,K)=C*EL(I,K)-S*EL(J,K)                                       BNSI 460
      EL(J,K)=D                                                         BNSI 470
40    CONTINUE                                                          BNSI 480
50    CONTINUE                                                          BNSI 490
60    M=M+1                                                             BNSI 500
C     CALCULATE DETERMINANT                                             BNSI 510
```

```
      DETERP=A(1,1)                                                     BNSI 520
      DO 70 I=2,N                                                       BNSI 530
70    DETERP=DETERP*A(I,I)                                              BNSI 540
      DETERM=DETERP                                                     BNSI 550
C     IS MATRIX SINGULAR                                                BNSI 560
      D=A(1,1)                                                          BNSI 570
      E=A(1,1)                                                          BNSI 580
      DO 80 I=2,N                                                       BNSI 590
      IF (DABS(D).LT.DABS(A(I,I))) D=A(I,I)                             BNSI 600
      IF (DABS(E).GT.DABS(A(I,I))) E=A(I,I)                             BNSI 610
80    CONTINUE                                                          BNSI 620
      EPSILP=EPSIL                                                      BNSI 630
      IF (EPSILP.EQ.0.) EPSILP=1.D-10                                   BNSI 640
      IF (D.EQ.0.) GO TO 190                                            BNSI 650
      IF (DABS(E/D).LT.DABS(EPSILP)) GO TO 190                          BNSI 660
C     INVERT TRIANGULAR MATRIX                                          BNSI 670
      J=N                                                               BNSI 680
      DO 120 J1=1,N                                                     BNSI 690
      LGT=1                                                             BNSI 700
      I=J                                                               BNSI 710
      DO 110 I1=1,J                                                     BNSI 720
      IF (LGT.EQ.0) GO TO 90                                            BNSI 730
      LGT=0                                                             BNSI 740
      IF (A(I,I).EQ.0.0) GO TO 200                                      BNSI 750
      A(I,J)=1.0D0/A(I,I)                                               BNSI 760
      GO TO 110                                                         BNSI 770
90    KS=I+1                                                            BNSI 780
      D=0.0D0                                                           BNSI 790
      DO 100 K=KS,J                                                     BNSI 800
100   D=D+A(I,K)*A(K,J)                                                 BNSI 810
      IF (A(I,I).EQ.0.0) GO TO 200                                      BNSI 820
      A(I,J)=-D/A(I,I)                                                  BNSI 830
```

```
110   I=I-1                                                         BNSI 840
120   J=J-1                                                         BNSI 850
C     PREMULTIPLY EL BY INVERTED TRIANGULAR MATRIX                  BNSI 860
      M=1                                                           BNSI 870
      DO 150 I=1,N                                                  BNSI 880
      DO 140 J=1,N                                                  BNSI 890
      D=0.0D0                                                       BNSI 900
      DO 130 K=M,N                                                  BNSI 910
130   D=D+A(I,K)*EL(K,J)                                            BNSI 920
      EL(I,J)=D                                                     BNSI 930
140   CONTINUE                                                      BNSI 940
150   M=M+1                                                         BNSI 950
C     RECOPY EL TO A                                                BNSI 960
      DO 160 I=1,N                                                  BNSI 970
      DO 160 J=1,N                                                  BNSI 980
160   A(I,J)=EL(I,J)                                                BNSI 990
170   ITEST=0                                                       BNSI1000
180   RETURN                                                        BNSI1010
190   ITEST=1                                                       BNSI1020
      GO TO 180                                                     BNSI1030
200   ITEST=-1                                                      BNSI1040
      GO TO 180                                                     BNSI1050
      END                                                           BNSI1060
      SUBROUTINE POL (F,FCALC,NP,IDENT)                             POL   10
C     PLOT PS ANN. TIME SPECTRUM:THEORETICAL AND EXP. RESULTS       POL   20
      DIMENSION X(512), Y(1024)                                     POL   30
      DOUBLE PRECISION F(512),FCALC(512)                            POL   40
      IA=NP+1                                                       POL   50
      IB=2*NP                                                       POL   60
      IC=1                                                          POL   70
      DO 10 I=1,NP                                                  POL   80
      X(I)=I                                                        POL   90
```

```
10    CONTINUE                                                          POL  100
      DO 20 I=1,NP                                                      POL  110
      Y(I)=F(I)                                                         POL  120
20    CONTINUE                                                          POL  130
      DO 30 J=IA,IB                                                     POL  140
      Y(J)=FCALC(J-NP)                                                  POL  150
30    CONTINUE                                                          POL  160
      DO 40 J=1,IB                                                      POL  170
      IF (Y(J).LT.1.0) Y(J)=1.0                                         POL  180
      Y(J)=ALOG(Y(J))                                                   POL  190
40    CONTINUE                                                          POL  200
      CALL SCALE (X(IC),NP,7.0,XMIN,DX,1)                               POL  210
      CALL SCALE (Y(IC),IB,4.0,YMIN,DY,1)                               POL  220
      CALL PLOT (2.0,2.0,-3)                                            POL  230
      CALL AXIS (0.0,0.0,14HCHANNEL NUMBER,14,-7.0,0.0,XMIN,DX)         POL  240
      CALL AXIS (0.0,0.0,14H   LOG(COUNTS),-14,-4.0,90.0,YMIN,DY)       POL  250
      CALL PLOT (0.0,4.0,3)                                             POL  260
      CALL PLOT (7.0,4.0,2)                                             POL  270
      CALL PLOT (7.0,0.0,2)                                             POL  280
      CALL SYMBOL (5.0,3.5,.25,IDENT,0.0,4)                             POL  290
      CALL PLOT (0.0,0.0,3)                                             POL  300
      DO 50 I=1,NP                                                      POL  310
50    CALL SYMBOL (X(I),Y(I),.1,2,0.,-1)                                POL  320
      CALL PLOT (0.0,0.0,3)                                             POL  330
C     PLOT OF F(CALC) WILL COME HERE                                    POL  340
      I=IA                                                              POL  350
      CALL LINE (X(I-NP),Y(I),NP,1)                                     POL  360
      CALL PLOT (120.0,-1.0,-3)                                         POL  370
      RETURN                                                            POL  380
      END                                                               POL  390
      SUBROUTINE INTENS (IDENT,NAME,BGD,STX,NC,NP,AA,SLOP,YCAL,OMIT)    INTS  10
C     INTENSITY CALC                                                    INTS  20
```

```
C     BGD IS THE COUNTER BACKGROUND FOR SUBTRACTION
C     STX IS THE NUMBER OF CHANNELS BETWEEN ZERO CHANNEL AND
C     FIRST DATA CHANNEL FOR CALC TAU
C     NC IS THE NUMBER OF COMPONENTS
C     NP IS THE NUMBER OF DATA PTS USED IN CALC TAU FOR COMP
C     AA IS THE COMP INTERCEPT VALUES AT ZERO TIME
C     SLOP IS THE COMPONENT SLOPES
C     YCAL IS THE THEORETICAL VALUES FOR NP DATA POINTS
C     YEXP IS THE EXPERIMENTAL VALUES FOR NEP DATA PTS ON
C     LEFT SIDE OF SPECTRUM FOR DETERMING TOTAL AREA UNDER CURVE
      DIMENSION NAME(11), AA(5), SLOP(5), YCAL(512)
      DIMENSION YEXP(200), XX(512), AREXP(5), TEN(5), AT(5)
      INTEGER OMIT
      READ (5,280) NEP,CONTR
C     NEP IS THE NO. OF ADDITIONAL EXPERIMENTAL GRAPH PTS NEEDED
C     TO CALC COMPONENT INTENSITIES
      IF (CONTR.NE.0) GO TO 10
      READ (5,290) (YEXP(I),I=1,NEP)
      GO TO 20
10    READ (5,300) (YEXP(I),I=1,NEP)
20    DO 30 I=1,NEP
      YEXP(I)=YEXP(I)-BGD
30    CONTINUE
      IE=I
C     PTST TEST
      XX(1)=STX
      DO 40 I=2,NP
      XX(I)=XX(I-1)+1.0
40    CONTINUE
      L=0
50    L=L+1
      DT=(-SLOP(NC)*XX(L))
```

```
      P=AA(NC)*EXP(DT)                                                  INTS 350
      PTST=YCAL(L)-P                                                    INTS 360
      IF (PTST.GT.5.0) GO TO 50                                         INTS 370
      PYS=YCAL(L)                                                       INTS 380
      PXS=XX(L)                                                         INTS 390
      J=IE+L                                                            INTS 400
C     CHANGE OF SUBSCRIPTS TO UNIFY THE DATA ORDER                      INTS 410
      DO 60 I=1,L                                                       INTS 420
      IE=IE+1                                                           INTS 430
      TEMP=YCAL(I)                                                      INTS 440
      YEXP(IE)=TEMP                                                     INTS 450
60    CONTINUE                                                          INTS 460
C     OUTPUT 1                                                          INTS 470
      WRITE (6,310) IDENT,NAME                                          INTS 480
      WRITE (6,320) NP,NC,BGD,STX                                       INTS 490
      WRITE (6,330) (I,AA(I),I,SLOP(I),I=1,NC)                          INTS 500
70    GO TO (80,90,80,90), OMIT                                         INTS 510
80    WRITE (6,340)                                                     INTS 520
      WRITE (6,350) (I,YEXP(I),I=1,J)                                   INTS 530
C     TOTAL AREA UNDER CURVE(ARSM)                                      INTS 540
C     ADJUSTMENT OF THE INDEX J                                         INTS 550
90    ODD=0.0                                                           INTS 560
      EVEN=0.0                                                          INTS 570
      KJ=0                                                              INTS 580
      KI=0                                                              INTS 590
      NEV=J-1                                                           INTS 600
      DO 100 I=2,NEV,2                                                  INTS 610
      KJ=KJ+1                                                           INTS 620
      EVEN=EVEN+YEXP(I)                                                 INTS 630
100   CONTINUE                                                          INTS 640
      NOD=J-2                                                           INTS 650
      DO 110 I=3,NOD,2                                                  INTS 660
```

```
      KI=KI+1
      ODD=ODD+YEXP(I)
110   CONTINUE
C     CALCULATION OF AREA
      JK=KJ+KI+2
      IF (JK-J) 120,140,120
120   J=J-1
      DO 130 JK=1,J
      YEXP(JK)=YEXP(JK+1)
130   CONTINUE
      GO TO 70
140   ARSM=0.33333*1.0*(YEXP(1)+2.0*EVEN+4.0*ODD+YEXP(J))
      TA=(-SLOP(NC)*PXS)
      ARTA=(AA(NC)*EXP(TA))/(SLOP(NC))
      ARSM=ARSM+ARTA
      WRITE (6,360) ARSM,ARTA,J,PTST,PXS,PYS
C     SUM OF COMPONENT AREAS(SUM)
      SUM=0.0
      DO 150 I=1,NC
      AREXP(I)=AA(I)/(SLOP(I))
      SUM=SUM+AREXP(I)
150   CONTINUE
      DO 160 I=1,NC
      TEN(I)=AREXP(I)/SUM
160   CONTINUE
      WRITE (6,340)
      WRITE (6,370) SUM
      WRITE (6,380) (I,TEN(I),I,AREXP(I),I,AA(I),I=1,NC)
C     OPTIMIZATION OF ZERO LINE
      T=0.0
      ADD=0.1
170   SUM=0.0
```

```
      T=T+ADD                                                           INTS 990
      IF (T.GT.STX) GO TO 270                                           INTS1000
      DO 180 I=1,NC                                                     INTS1010
      AT(I)=AA(I)*EXP(-SLOP(I)*T)                                       INTS1020
      AREXP(I)=AT(I)/SLOP(I)                                            INTS1030
      SUM=SUM+AREXP(I)                                                  INTS1040
  180 CONTINUE                                                          INTS1050
      IF (SUM-ARSM) 190,240,170                                         INTS1060
  190 IF (ABS((SUM-ARSM)/ARSM).LT.0.01) GO TO 240                       INTS1070
      T=T-ADD                                                           INTS1080
      ADD=ADD/10.0                                                      INTS1090
      IF (ADD.LE.0.0001) GO TO 200                                      INTS1100
      GO TO 170                                                         INTS1110
  200 T=0.0                                                             INTS1120
      SUB=-0.1                                                          INTS1130
  210 SUM=0.0                                                           INTS1140
      T=T+SUB                                                           INTS1150
      DO 220 I=1,NC                                                     INTS1160
      AT(I)=AA(I)*EXP(-SLOP(I)*T)                                       INTS1170
      AREXP(I)=AT(I)/SLOP(I)                                            INTS1180
      SUM=SUM+AREXP(I)                                                  INTS1190
  220 CONTINUE                                                          INTS1200
      IF (SUM-ARSM) 210,240,230                                         INTS1210
  230 IF (ABS((SUM-ARSM)/ARSM).LT.0.01) GO TO 240                       INTS1220
      T=T-SUB                                                           INTS1230
      SUB=SUB/10.0                                                      INTS1240
      IF (SUB.LE.0.0001) GO TO 240                                      INTS1250
  240 DO 250 I=1,NC                                                     INTS1260
      TEN(I)=AREXP(I)/SUM                                               INTS1270
  250 CONTINUE                                                          INTS1280
C     OUTPUT 2                                                          INTS1290
      WRITE (6,340)                                                     INTS1300
```

```
      WRITE (6,390) SUM,T                                               INTS1310
      WRITE (6,400) (I,TEN(I),I,AREXP(I),I,AT(I),I=1,NC)                INTS1320
      WRITE (6,410)                                                     INTS1330
      DO 260 I=1,NC                                                     INTS1340
  260 TEN(I)=TEN(I)*100.0                                               INTS1350
      WRITE (6,420) (TEN(I),I=1,NC)                                     INTS1360
  270 RETURN                                                            INTS1370
C                                                                       INTS1380
  280 FORMAT (2I5)                                                      INTS1390
  290 FORMAT (F6.0,9F7.0)                                               INTS1400
  300 FORMAT (F9.0,7F10.0)                                              INTS1410
  310 FORMAT (1H1,3X,A4,11A4)                                           INTS1420
  320 FORMAT (//5H  NP=,I3,5H  NC=,I2,6H  BGD=,F10.5,6H  STX=,F5.2//)   INTS1430
  330 FORMAT (5X,2HA(,I2,2H)=,F15.5,7H  SLOP(,I2,2H)=,F12.8)            INTS1440
  340 FORMAT (1H0)                                                      INTS1450
  350 FORMAT (9H    YEXP(,I2,2H)=,F15.5,9H    YEXP(,I2,2H)=,F15.5,9H    INTS1460
     1YEXP(,I2,2H)=,F15.5,9H    YEXP(,I2,2H)=,F15.5)                    INTS1470
  360 FORMAT (//10X,5HARSM=,E15.8,7H  ARTA=,E15.8,4H  J=,I3,7H  PTST=,F1INTS1480
     10.5,6H  PXS=,F8.4,6H  PYS=,F10.5)                                 INTS1490
  370 FORMAT (15X,4HSUM=,E15.8)                                         INTS1500
  380 FORMAT (10X,2HI(,I2,2H)=,E15.8,5X,8H  AREXP(,I2,2H)=,E15.8,5X,4H  INTS1510
     1A(,I2,2H)=,F12.5)                                                 INTS1520
  390 FORMAT (15X,4HSUM=,E15.8,4H  T=,F10.5)                            INTS1530
  400 FORMAT (10X,2HI(,I2,2H)=,E15.8,5X,8H  AREXP(,I2,2H)=,E15.8,5X,5H  INTS1540
     1AT(,I2,2H)=,F12.5)                                                INTS1550
  410 FORMAT (////111H                                       1ST COMP   INTS1560
     1     2ND COMP        3RD COMP        4TH COMP        5TH COMP)    INTS1570
  420 FORMAT (//5X,15HINTENSITY   (%),9X,5F16.3)                        INTS1580
      END                                                               INTS1590
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THE REACTION OF ORTHO-POSITRONIUM WITH NITROAROMATICS

by

William Juul Madia

(ABSTRACT)

A study was made to ascertain the mechanism by which ortho-positronium reacts with nitroaromatics in solution. These reactions are two to three orders of magnitude faster than expected by simple pickoff. Conjugation of the nitro group with the aromatic ring was found to be a necessary condition for this behavior. The rate constant for each of these reactions was measured in suitable solvents over a wide temperature range, 200-500°K. Distinct departure from the Arrhenius law was found. In general, the rate constant increased linearly with increasing temperature up to a point, and then decreased linearly as the temperature was raised further. The following mechanism is postulated:

$$\mathrm{Ps} + \mathrm{M} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{PsM} \xrightarrow{k_2} \mathrm{M} + 2\gamma$$

Ortho-Positronium reacts with the nitroaromatic, M, to form a complex in a reversible step. The complex may either decompose into a positronium atom and nitroaromatic molecule or it may go on to annihilate the positron. A steady-state

concentration of the complex is assumed and the observed rate constant for the process is

$$k_{obs} = \frac{k_1 k_2}{k_{-1} + k_2}$$

The two limiting cases are: (1) $k_2 >> k_{-1}$ causing $k_{obs} \simeq k_1$. Typical Arrhenius behavior is expected and observed in this region, and (2) $k_{-1} >> k_2$ causing $k_{obs} \simeq K_{EQ} k_2$. In this region $H_{EQ} + E_a(2) <0$ and the observed rate constant decreases with increasing temperature. This corresponds to a stable but temperature sensitive PsM complex.

An approximate molecular orbital study has been made to study the possible existence of positron and positronium complexes with a select number of organic molecules. The CNDO/2 approximation is used for all electronic integrals and for electron positron Coulomb integrals. The core Hamiltonian matrix elements for the positron were estimated by combining the Wolfsberg-Helmholtz and Cusachs-Cusachs approximations. This approach shows that the positron should become bound to the molecules. Using the same criteria, the formation of stable positronium complexes is more improbable. The calculated binding energies are strongly dependent on the value of the Wolfsberg-Helmholtz proportionality constant for positrons.