Temperature, Pressure & Solvent Dependence of Positronium Acceptor Reactions

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PACS No.: 82.55.+e,71.60.+z, 78.70.Bj

Abstract

Positronium (Ps) reaction rates ($\kappa$) with weak Acceptors (Ac) leading to the formation of Ps-Ac Complexes show several intriguing features: non-monotonic temperature dependence of $\kappa$ (departing from the usual Arrhenius paradigm), considerable variability of $\kappa$ with respect to different solvents, and anomalies in response to external pressure at ambient temperature (large changes of $\kappa$ in some media and hardly any in others). We explain all these phenomena, introducing the novel concept of a critical surface tension, which unifies observations in diverse non-polar solvents at different temperatures and pressures.

The Positronium (Ps) atom, as the ‘lightest isotope of hydrogen’, enters into various chemical reactions, amongst which we shall concentrate here on those with diamagnetic organic compounds (equipped with a suitable low-lying molecular orbital) such that a Positronium-Acceptor (Ps-Ac) Complex can form in the presence of some solvent (S).

The observed rate constant ($\kappa$) for a given Acceptor depends on the solvent and for a given solvent varies in a rather remarkable manner with temperature ($T$), namely:

- $\kappa$ increases with $T$ at low temperatures,
- $\kappa$ reaches a maximum at $T = T_0$ (the turnover temperature),
- $\kappa$ decreases with increasing $T$ above $T_0$.

This is shown in Fig.1 for the case of the weak Acceptor nitrobenzene in different solvents.

![Fig.1](image)

**Fig.1** Observed temperature dependence of rate constants for Ps reaction with nitrobenzene in different solvents. (Taken from W.D.Madia et.al., J.Am.Chem.Soc. 97(1975)5041). The lines correspond to slopes in the enthalpy dominated and diffusion controlled regimes as predicted by our model(with appropriate over-all normalization for heptane).

This unusual phenomenon [1], first observed by Goldanskii and his group [2] at Moscow, and subsequently by Hall, Madia and Ache [3], is in sharp contrast with the normal trend in
activated chemical processes where $\ln \kappa$ versus $1/T$ (the inverse temperature) yields a straight line with negative slope, as the rate is proportional to the Maxwell-Boltzmann probability factor $\exp(-E^*/k_BT)$ where $k_B$ is the Boltzmann constant and $E^*$ is the activation energy or barrier height to be overcome by thermal agitation. Possible prefactors are generally taken to be mildly dependent on temperature.

Another dramatic observation [4,5] pertains to the variation of the rate constant for Ps-Ac Complex formation with external pressure at ambient temperature, which shows surprisingly strong solvent dependence. Thus, for instance, with nitrobenzene as the Acceptor and hexane as the solvent the rate constant $\kappa$ was found to be enhanced by a factor of almost thirty as the pressure was increased to $\sim 1000$ kg/cm$^2$, while with benzene as the solvent the same rate manifested only small variation over the same pressure range. This feature is depicted in Fig.2. Kobayashi [4,5] conjectured that this could indicate a difference in reaction mechanism in cases which do and those which do not show marked pressure dependence, and that a correlation could be sought with the corresponding solvent dependence of the turnover temperature.

![Fig.2 Observed dependence on external pressure for Ps reaction with nitrobenzene in hexane and in benzene. The predicted dependence in the case of hexane is shown by the solid line (appropriate normalization has been done).](image)

The objective of this letter is to put forward a heuristic model which captures the essence of all these puzzling aspects of Positronium reactions outlined above, through a remarkably simple and reasonably accurate semi-quantitative description. As we shall see, the widely used bubble model for Ps-annihilation in liquids provides a suitable setting for the purpose at hand. This was proposed by Ferrel [6] to account for the observed largeness of the ortho-Positronium (o-Ps) pick-off lifetime, whereby the positron in o-Ps seeks out an electron in the surrounding medium with opposite spin (not its partner in o-Ps which is in a spin triplet state) to decay into two gammas. He suggested that due to the repulsive interaction between o-Ps and the atoms of the surrounding liquid, the Positronium pushes away the molecules of the liquid and gets self-trapped in a cavity or bubble. The decreased probability for the positron to find an electron (of the surrounding medium) in its immediate vicinity leads to the lengthening of the pick-off lifetime. For simplicity he took the trapping potential to be an infinitely repulsive spherical well of radius $R$. The resulting quantal zero-point energy of Ps with mass $2m$ ($m$ being the electron mass) is $E_0 = \frac{\pi^2\hbar^2}{4mR^2}$. This exerts an outward ‘pressure’ viz. $-\frac{\partial E_0}{\partial R}$ to be balanced by the contractile forces of compression due to the surface tension ($\sigma$) of the fluid, thereby minimizing the total energy $E_{tot} = E_0 + 4\pi R^2 \sigma$ viz. $\frac{\partial E_{tot}}{\partial R} = -\frac{2\pi^3}{4mR} + 8\pi R \sigma = 0$ resulting in a bubble of radius $R_0 = \left(\frac{\pi^2\hbar^2}{16m\sigma}\right)^{1/4} = \left(12.445\right)/\sigma^{1/4}\text{Å}$, where $\sigma$ is measured in dynes/cm ($0.624 \times 10^{-4}$ eV/Å$^2$).
This model was further developed by Tao [7] and by Eldrup et al. [8] employing again the infinite spherical well but describing the picked-off electrons as forming a thin layer uniformly coating the inner surface of the bubble. Though such a description has been criticised on account of the infinite repulsion [9,10] or the unrealistic nature of the sharpness of the bubble edge [11,12], nevertheless as a first approximation the model does rather well in explaining the observables in the case of pure solvents (lifetime and angular correlation of decay gammas).

In this framework the formation of the Ps-Ac Complex within the cavity results, through the restriction on the motion of the Positronium due to its binding to the Acceptor, in a release of the outward ‘uncertainty pressure’ and accordingly the bubble begins to shrink under the influence of the surface tension. As the bubble wall approaches the Positronium (bound to the Acceptor with some energy $E = -B$ where $B$ is the binding energy), the increasing proximity of the solvent molecules leads (because of the augmented repulsive energy) to a reduction of the binding, until at some radius $R_b$ of the bubble the Ps-Ac bond is broken viz. $B = 0$. To raise the status of this contention [13] to at least a semi-quantitative level let us consider the Positronium to be subjected to an attractive potential $V(r)$ due to the Acceptor, while it also feels the infinite repulsion due to the solvent located at the bubble wall at a distance $R$. Taking the potential $V(r)$ to be a spherical well [14] of depth $V_0$ and range $a$ viz. $-V_0\Theta(a-R)$ where $\Theta$ is the step function, the relevant Schrödinger equation for the centre-of-mass motion of Ps is

\[
\begin{align*}
\left[-\frac{\hbar^2}{4m}\frac{d^2}{dr^2} - V_0\right]u &= -Bu \quad \text{for} \quad r < a \\
\left[-\frac{\hbar^2}{4m}\frac{d^2}{dr^2}\right]u &= -Bu \quad \text{for} \quad r > a
\end{align*}
\]

(1a)

(1b)

with $\psi = u/r$. The appropriate boundary conditions are $u(r = 0) = 0$ and $u(r = R) = 0$, while $u$ and its derivative must be continuous at $r = a$, yielding the eigenvalue condition

\[ k\tan\kappa a = -\kappa \tanh k(R-a) \]

(2)

where $k = \sqrt{\frac{4mV_0}{\hbar^2}}$ and $\kappa = \sqrt{\tilde{g}^2 - k^2}$ with $\frac{4mV_0}{\hbar^2} = \tilde{g}^2$. The bond breaking radius $R_b$, viz. where $k = 0$, is thus given by

\[ R_b = a\left[1 - \frac{\tan \tilde{g}a}{\tilde{g}a}\right]. \]

(3)

Since in the leading approximation (adopted by us) the effect of the solvent is represented by an infinite repulsion (tantamount to a boundary condition forcing $\psi$ to vanish at $R$), the radius $R_b$ depends only on the characteristics of the Acceptor vis a vis its affinity for the Positronium, and is, to that extent, same for all solvents. However, we must also consider the fact that the Ps-Ac-bubble system would equilibrate at some radius $R_{min}$ at which the total energy is a minimum, namely,

\[ \frac{\partial}{\partial R}[-B + 4\pi R^2\sigma] = 0. \]

(4)

This leads to

\[ R_{min} = (\frac{1}{8\pi\sigma})(\frac{\hbar^2}{4m})(\frac{1}{a^4})\frac{6\zeta^4}{(\zeta - \tan \zeta)(3\zeta - 3\tan \zeta + 3\zeta \tan^2 \zeta - 2\tan^3 \zeta)} \]

(5)

where $\zeta \equiv \tilde{g}a$. Whether the Ps-Ac-bubble system will be stable or not will depend on whether $R_{min}$ is greater than or lesser than the bond-breaking radius $R_b$.

A big step forward is made possible by our recognition that in leading approximation $R_b$ is essentially solvent independent, while solvent dependence enters through $R_{min}$ and that too only through $\sigma$. As the surface tension of the solvent is a function of temperature, the equilibrium radius of the bubble (with Ps-Ac inside) depends on temperature only through $\sigma$ viz. $R_{min}(T) = R_{min}[\sigma(T)]$. As $T$ is decreased, $\sigma$ increases and by virtue of eq.(4) and more
explicitly eq.(5), $R_{\text{min}}$ decreases. When $R_{\text{min}}$ becomes less than $R_b$ the Ps-Ac-bubble system is no longer stable. Clearly there is a critical value of $\sigma$, say $\sigma_{cr}$, at which $R_{\text{min}}[\sigma_{cr}] = R_b$, marking the watershed beyond which the Ps-Ac-bubble system destabilises. The value of $T$ at which $\sigma$ attains the value $\sigma_{cr}$ depends on the particular solvent, but $\sigma_{cr}$ does not, but is, in the leading order, a property of the Acceptor under consideration. We argue that the turnover temperature $T_0$ is the temperature at which, for the solvent at hand, $\sigma(T_0) = \sigma_{cr}$. Indeed at sufficiently high temperature where $\sigma(T) < \sigma_{cr}$, a large negative change in enthalpy occurs as the reactants [Ps in a bubble of radius $R_0 = (\frac{\pi h^2}{16m\sigma})^{1/4}$ and the Acceptor] react to form the product [Ps-Ac Complex in bubble] with the radius having shrunk to $R_{\text{min}}$. This makes it a down-hill reaction, since for weak Acceptors the activation energy is expected to play a sub-dominant role and also the effect of solvent viscosity is negligible (because the complex is protected by the bubble from the buffetting by the solvent molecules). It is thus basically the negative activation volume that is responsible for the anti-Arrhenius behaviour for $T > T_0$. On the other hand for $T < T_0$ when $\sigma(T) > \sigma_{cr}$ the Ps-Ac-bubble system is unstable, the Ac is squeezed out of the bubble and the formation of the Complex must of necessity take place in the milieu of the solvent accompanied by the continual impact of the solvent molecules. As such, following Kramers [15] the role of the medium would be said to belong to the Smolochowski regime, with the dependence of the rate constant on the viscosity ($\eta$) varying as $\frac{1}{\eta^2} \sim D$ (where $D$ is the diffusion coefficient of the liquid, the last step being a consequence of the Einstein-Stokes relation). In view of the smallness of the activation energy for weak Acceptors, we would therefore expect that $\kappa \sim \exp[-E_\eta/k_BT]$, where $E_\eta$ is the activation energy associated with the process of diffusion. The reaction in this region would be diffusion controlled and would exhibit a normal Arrhenius behaviour. This enables us to make the important prediction that $\sigma(T_0) = \sigma_{cr}$ and that it is approximately solvent independent. In order to confront this with experiment, we have plotted in Fig.3, $\sigma(T)$ against $T - T_0$ for various solvents (for which data is available with nitrobenzene as the Acceptor).

\[\text{Fig.3 Surface tension } \sigma(T) \text{ for different solvents as a function of } T - T_0 \text{ exposing the concept of the critical surface tension } (\sigma_{cr})\]

It is indeed highly gratifying to note that while $T_0$ differs widely from solvent to solvent, and also the values of the surface tension $\sigma$ at a given temperature for different solvents have a substantial spread, nevertheless $\sigma(T_0) = \sigma_{cr}$ for the solvents under consideration lie in a rather narrow range, namely, $\sigma_{cr} = 26 \pm 2$ dynes/cm.

Armed with this value of $\sigma_{cr}$ we are now in a position to access the Ps-Ac interaction parameters which, as we shall discuss below, are unfortunately not available from any other
source. Being led by the estimates of other authors [16] let us fix the range of the interaction to be $a = 1.5 \ \text{Å}$, and determine $\tilde{g}$ by putting, in accordance to our discussions above, $\sigma = \sigma_{cr}$ and $R_{\text{min}} = R_0$ [refer eq.(3)]. This immediately yields the value $\tilde{g} = 1.25 \ \text{Å}^{-1}$ which corresponds to the Ps-Ac binding energy (the Acceptor being nitrobenzene) $B_0 = 0.18 \text{eV}$. Note that $B_0$ signifies the basic binding in the absence of the solvent, namely, $B_0 = \text{Lim}_{R \to \infty} B$, which implies vide eq.(2), the well-known result: $-\kappa \cot \kappa a = k$ the eigenvalue condition for a spherical well. Unfortunately there is no direct measurement of this binding energy $B_0$, and the approaches based on first principles [17] are beset with huge theoretical uncertainties. However, using our methodology we have now completely tied down the model and shall proceed to show how this explains all the main observed features.

In order to find the slope of the $\ln \kappa$ versus $1/T$ plot in the higher temperature anti-Arrhenius region we recognise that this is nothing but the activation free energy, the major contribution to which come from the change in Enthalpy arising from the shrinkage of the bubble from its value given by $R_0$ to the size determined by $R_{\text{min}}$, viz. $4\pi R_{\text{min}}^2 \sigma - 4\pi R_0^2 \sigma$ where, of course the radii are functions of temperature through the surface tension. To this must be added the change in the Ps-Ac binding due to the approach of the bubble wall from $R_0$ to $R_{\text{min}}$. The resulting behaviour (appropriately normalized) is depicted in Fig.1 for the case of Ps nitrobenzene reaction in heptane, for instance, as a solvent. The slope obtained through our model corresponds to $\approx 0.15 \text{eV}$ which agrees very well with the experimental value. The part of the plot in the Arrhenius regime is also shown by using the value of the activation energy for diffusion ($E_\eta$). Fig.1 demonstrates that the main aspect of the temperature dependence of the rate has been captured in a satisfactory manner.

Apart from providing an interpretation of the temperature dependence of the reaction as set forth above, this simple model is also able to furnish an explanation of the observed variation with the external pressure ($P$). In view of the small compressibility of liquids one would hardly expect any appreciable activation volume when $T < T_0$ as the reaction occurs in the solvent itself. However, for $T > T_0$ due to the involvement of the bubble a large $\Delta V^*$ (activation volume) becomes possible and hence a significant pressure dependence can occur, in view of the basic Polányi relationship:

$$
\left( \frac{\partial \ln \kappa}{\partial P} \right)_T = \frac{\Delta V^*}{k_B T}
$$

between the effect of external pressure on the rate of a chemical reaction and the activation volume of the reaction (namely, the difference between the volume of the activated complex and the volume of the reactants). To obtain quantitative estimates it is to be noted that the initial volume viz. Ps in the bubble without the Ac must be found now by minimizing the total energy, namely $E_{\text{tot}} = \frac{k^2}{4m R^2} + 4\pi R^2 \sigma + \frac{4\pi}{3} R^3 P$ with respect to $R$ and thereby obtain $R_0(P)$. Here $P$ is measured in kgwt/cm$^2$ ($=6.13 \times 10^{-6} \text{ eV/Å}^3$). Similarly the equation determining the equilibrium radius $[R_{\text{min}}(P)]$ with Ps-Ac inside the bubble must be appropriately modified, so that in place of eq.(4), we now have

$$
\frac{\partial}{\partial R}(-B + 4\pi R^2 \sigma + \frac{4\pi}{3} R^3 P) = 0
$$

Equipped with $R_0(P)$, $R_{\text{min}}(P)$ and $B[R(P)]$ the variation of the rate constant with pressure can be readily calculated.

Consider the two typical cases depicted in Fig.2 out of the many taken from the experimental studies of Kobayashi [4,5]. All these experiments were performed at ambient temperature ($T_{\text{expt}} = 19 \pm 1^\circ\text{C}$). With nitrobenzene as the Acceptor and benzene as the solvent we note that there is no significant effect of pressure on the reaction rate. This is quite consistent with the model in view of the fact that the turnover temperature in this case [18] is considerably above $T_{\text{expt}}$ and hence one is working in the Arrhenius region where the pressure effect is expected to be small. On the other hand when the solvent is hexane, the experiment was performed
in the regime where the Ps-Ac-bubble system is stable (as the turnover temperature here is \(-53^\circ C\)), and accordingly the reaction rate responds appreciably to external pressure. Indeed the enhancement of the rate by a factor of about thirty in our model is even in quantitative agreement with the experimental results of Kobayashi. Using the experimental value of the surface tension of hexane at \(T_{\text{expt}} \approx 19\) dynes/cm, the model indicates the behaviour shown in Fig.2 with appropriate over-all normalization.

Above a critical pressure the Ps-Ac-bubble system destabilizes and the rate versus pressure curve levels off. Except for the fact that there is a somewhat precocious onset of the Arrhenius regime the general experimental trend is captured very well indeed considering the approximations involved.

We may thus conclude that the simple model we have proposed effectively accounts for the temperature, pressure and solvent dependence of Ps-Ac Complex formation reactions. Of cardinal importance for our discussion has been the introduction of the notion of the critical surface tension (\(\sigma_{cr}\)) which enables us to semiquantitatively account for most observations and also to make the important qualitative remark: that for any solvent at a temperature such that its surface tension is smaller than \(\sigma_{cr}\) the reaction rate decreases with increasing temperature and is also significantly affected by external pressure, while otherwise it is the other way around.

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[18] Indications are already there in reference 2 but very careful measurements recently made in our laboratory place the turnover temperature for Ps-nitrobenzene reaction with benzene as a solvent at \(33 \pm 3^\circ C\).