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Temperature, Pressure and Solvent Dependence of Positronium Reactivity toward Nitrobenzene

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Positronium (Ps) reaction rates, with weak acceptors(Ac) (such as nitrobenzene) leading to the formation of Ps−Ac complexes, have long been known to exhibit intriguing features: nonmonotonic temperature dependence (at variance with the usual Arrhenius behavior), considerable variation in characteristics with different solvents, and anomalies with respect to external pressure at ambient temperature (large changes in some media and hardly any in others). We present precise measurements performed in our laboratory on the temperature dependence of the reaction rate (κ) for Ps toward nitrobenzene in benzene as the solvent, determining in particular, the "turnover point" (or rather the region) carefully, a result which when taken in juxtaposition with earlier experimental findings by Kobayashi, vis-a-vis external pressure dependence of the rate in benzene versus other solvents, enables us to provide a natural semiquantitative explanation in the context of the bubble model of Ps in liquids.

1. Introduction

The Positronium (Ps) atom, as the lightest "isotope" of hydrogen, enters into various chemical reactions among 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 milieu of some solvent S. The signal for complex formation is the enhancement in the rate for pick-off annihilation of the long-lived (spin triplet) ortho-positronium (*o*-Ps) state, whereby the positron in *o*-Ps seeks out an electron in the surrounding medium (not its partner in Ps) with opposite spin and decays into two gammas (2γ). In the pure solvent S, suppose this pick-off annihilationa rate is $\lambda_p{}^0$. With the formation of the complex the pick-off annihilation (λ_p) is enhanced (viz., the lifetime $\tau_p = 1/\lambda_p$ is quenched) due to the proximity with the pick-off electron as Ps is ensconced in the binding location of the acceptor. This increase is, of course, proportional to the rate (κ) of the reaction for complex formation and the acceptor concentration [Ac]. Indeed

$$\lambda_p = \lambda_p^{(0)} + \kappa[\mathrm{Ac}] \tag{1}$$

The corresponding reaction scheme being

$$\mathrm{Ps}+\mathrm{Ac}+(\mathrm{S}) \rightleftharpoons (\mathrm{Ps}-\mathrm{Ac})+(\mathrm{S}) \rightarrow \mathrm{Ac}+2\gamma+(\mathrm{S}) \tag{2}$$

Thus the desired rate (κ) is readily determined by measuring the rate constant for the pickoff annihilation in the case of pure solvent (S) and for known concentrations of acceptor dissolved in S.

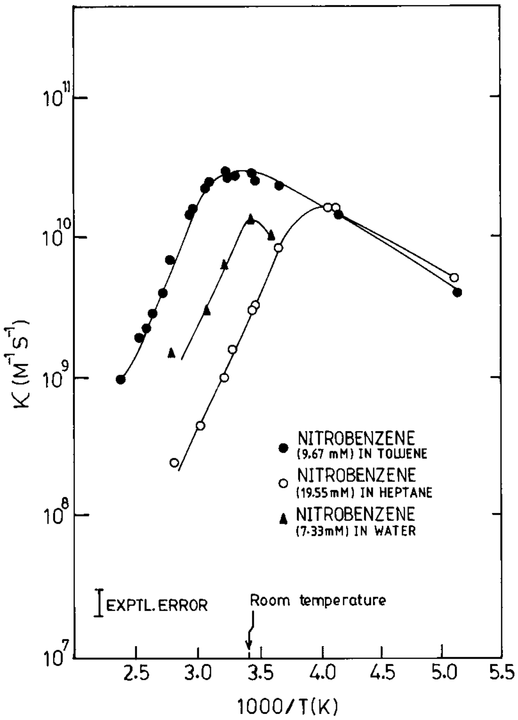

Figure 1. Observed temperature dependence of rate constant for the reaction $\mathrm{Ps} + \mathrm{Ac} + (\mathrm{S}) \rightleftharpoons \mathrm{Ps\text{-}Ac} + (\mathrm{S})$ in different solvents showing Arrhenius and anti-Arrhenius behavior and the turnover (taken from W. J. Madia et al., *J. Am. Chem. Soc.* **1975**, *97*, 5041; Hall, E. S.; Ache, H. J. *J. Inorg. Nucl. Chem.* **1978**, *40*, 1690).

This rate constant (κ) for a given acceptor depends on the solvent and for a given solvent varies in a rather remarkable manner with temperature, namely:

- κ increases with temperature (T) at low temperatures,
- κ reaches a maximum at $T = T_0$ (which shall be called the turnover temperature),
- κ decreases with temperature above T_0,

as can be seen from the Arrhenius plot, viz., ln κ vs ($1/T$) (the inverse of temperature) shown in Figure 1. This unusual phenomenon[1] was first reported by Goldanskii[2] and his group in Moscow and subsequently by Hall, Madia, and Ache.[3] This

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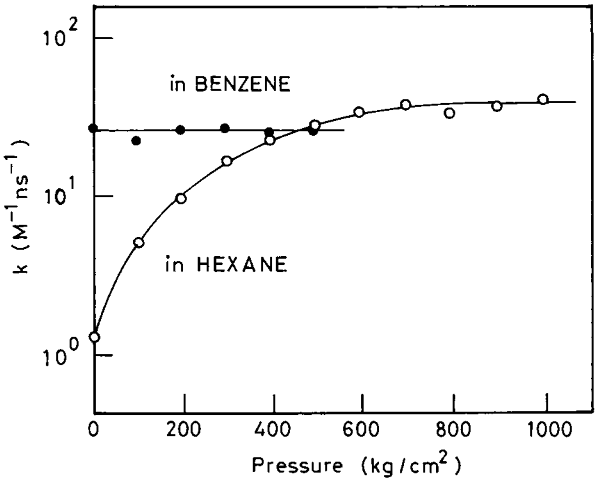

Figure 2. Pressure dependence of Ps-nitrobenzene complex formation rate constants in benzene and hexane as solvents (taken from ref 4).

behavior should be put in contrast with the usual trend in activated chemical processes where ln κ vs ($1/T$) yields a straight line with negative slope, a tendency readily explicable from the underlying basic mechanism whereby the reactants proceed toward the products of the reaction by crossing a barrier (of height E^* say) in the free energy with respect to some relevant reaction coordinate. As this is achieved by thermal agitation, the reaction rate is naturally proportional to the Maxwell−Boltzmann probability factor $exp(-E^*/k_BT)$, k_B being the Boltzmann constant. Possible prefactors are generally taken to be only mildly dependent on temperature.

Another surprising result that we owe to the experimental observations made by Kobayashi[4,5] pertains to the dependence of the rate constant κ for Ps-Ac complex formation on external pressure showing an amazing solvent dependence. Thus, for example, with nitrobenzene as the acceptor, when the medium was taken to be hexane the rate κ was found to undergo an enhancement of a factor of almost thirty when the pressure was increased from zero to ~1000 kg/cm^2, while with benzene as a solvent the same rate constant demonstrated very little variation over the same range of external pressure. This feature is depicted in Figure 2. These experiments were all performed at ambient temperature ($T_{\rm expt} = 19 \pm 1$ °C $= 292 \pm 1$ K). Guided by the basic relationship due to Evans and Polanyi[6]

$$\left(\frac{\partial \ln \kappa}{\partial P}\right)_T = -\frac{\Delta V^*}{k_B T} \tag{3}$$

between the effect of external pressure on the rate of a chemical reaction and the activation volume (ΔV^*) of the reaction (namely, the difference between the volume of the activated complex and the volume of the reactants), Kobayashi conjectured that this could indicate a difference in mechanism in the cases which do, and those that do not, show marked pressure dependence, and that a correlation could be sought with the rising and falling portions of the Arrhenius plot for the temperature variation.

The objective of the present study is 2-fold:

- As emphasized in ref 1, most of the available Ps quenching data were based on measurements made before 1975, and hence, the quality of the results is poorer than what can be obtained today. Results were extracted from lifetime spectra measured with resolution of 400 to 1200 ps. Furthermore, in most cases good computer programs for the reliable extraction of the pick-off component were not used, and sometimes two component fits (in place of generally adopted three) were employed. In particular, with benzene as a solvent, while good data is available for pressure dependence (Figure 2), the experimental status of the temperature dependence of Ps−nitrobenzene complex formation in benzene is somewhat ambiguous especially in connection with the all important turnover region. Indeed, data points in this case[2] have been taken in the rising anti-Arrhenius regime. Therefore, in the first place we present the results of careful measurements carried out in our laboratory (and a conservative assesment of the data) for the case of benzene as the solvent. This is described in the next section.
- Second, we put forward a heuristic model which captures essential aspects of these phenomena in a semiquantitative manner and this is included in the section devoted to results and discussion.

2. Experiment and Analysis

Chemicals. A spectroscopically pure sample of benzene from MERCK was used. Nitrobenzene procured from BDH of high grade purity was employed for experiments. The nitrobenzene concentration in the solution was ~6.8 mM. The low concentration of nitrobenzene is to keep the solvent properties intact (particularly so with benzene as the solvent).

Surface tension measurements were done in constant-temperature bath RET 111 Neslab, employing -du Nouy torsion balance method by the instrument KRÜSS Interfacial Tensiometer K8 (the error involved in this measurement was ±0.01 dynes/cm).

Positron Lifetime Measurement. The carrier-free positron source (^{22}Na in the form of NaCl) of strength ~5 μCi was deposited on a thin (400 μg/cm^2) Mylar film and sealed with another identical film on top of it, the edges of which were sealed together to render it leak proof. The source was put in a cylindrical container which contained the sample and was carefully degassed by the freeze−thaw technique. The source sample assembly maintained at a constant temperature (to within ±0.1 °C) by the bath was placed between the detectors. The positron annihilation lifetimes were measured with a slow−fast coincidence system. The detectors used were truncated cone-shaped (of dimension 25.4 mm diameter tapered to 12.7 mm diameter and of 25.4 mm height) spectroscopic quality BaF$_2$ scintillators (optically polished on all sides) coupled to Philips XP2020Q photomultiplier tubes. The resolving time (fwhm), measured with a ^{60}Co source and with the windows of the slow channels of the fast−slow coincidence assembly set to select pulses corresponding to 511 keV to 550 keV in one channel and 900 keV to 1350 keV in the other, was 183 ps. For each temperature setting, a total of ~10^6 coincidence counts (over a period of ~10 h) had been recorded with 4000:1 peak-to-random ratio. The lifetime spectra so obtained were analyzed with the PATFIT-88 program. The fwhm(resolution) obtained from the program RESOLUTION was used in the POSITRONFIT program, with a necessary source correction of 5%, to get the final analysis of the data. A best fit was obtained using three-components analysis. The measurements were mainly focused on the long-lived pick-off component. The fitting errors in measuring the lifetime, correspond to a standard deviation of ~1%.

The decay rates corresponding to the pick-off lifetime component for pure benzene ($\tau_p^0 = 1/\lambda_p^0$) on one hand and for solutions of nitrobenzene (at millimolar level concentration) in benzene ($\tau_p = 1/\lambda_p$) on the other, at different temperatures, were measured. In doing the experiment care was taken to avoid acquiring data close to the freezing temperature of benzene as

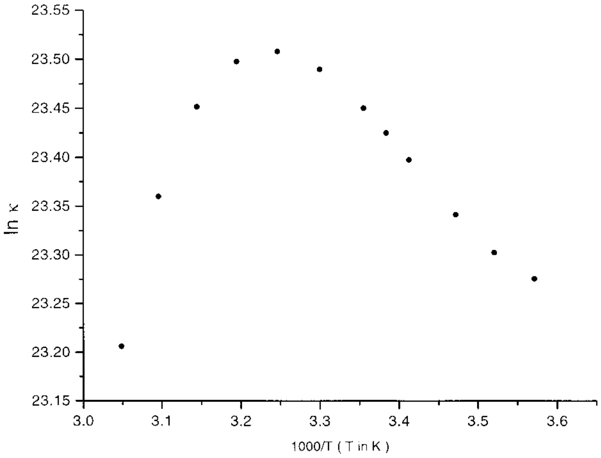

Figure 3. Temperature dependence of Ps-nitrobenzene reaction rate constant in benzene as observed by us, in our laboratory, with nitrobenzene concentration [Ac] = 6.8 mM/L.

clustering and other forms of association of molecules could introduce factors extraneous to our purpose.

A χ^2-fit was made to the data in the case of pure solvent (and the specimens with nitrobenzene dissolved therein) for λ_p^0 vs T (and λ_p vs T) using a polynomial of order three. From these fits the curve for ln κ vs $(1/T)$ was readily deduced using eq 1. The result is shown in Figure 3. The turnover region is determined through the flatness of the neighborhood of the maximum, as also from the variation of this feature with samples at different acceptor concentration. Careful and conservative estimates made by us reveal that the "turnover temperature" for Ps−nitrobenzene complex formation reaction with benzene as the solvent is situated at 33 ± 3 °*C*.

Discussion and Conclusion

We shall see below that the bubble model for positronium annihilation in liquids provides a suitable setting for the explanation of the enigmatic features described in the Introduction and reinforced by our experiment. This model was proposed by Ferrel[7] to account for the observed largeness of the *o*-Ps lifetime for the pick-off process. He suggested that due to the repulsive electron exchange 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 a bubble. The decreased probability for the positron to find an electron 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 resultant quantal zero-point energy of the positronium with mass $2m$ (m being the electron mass) is accordingly given by

$$E_0 = \frac{\pi^2\hbar^2}{4mR^2} \tag{4}$$

which in turn exerts a "pressure" $-(\partial E_0)/(\partial R)$ to be balanced by the forces of compression due to the surface tension (σ) of the fluid. Thus minimizing the total energy in the absence of appreciable external pressure (neglecting a possible term $^4/_3\pi R^3 P_{ext}$)

$$E_{tot} = E_0 + 4\pi R^2\sigma \tag{5a}$$

viz.,

$$\frac{\partial E_{tot}}{\partial R} = -\frac{2\pi^2\hbar^2}{4mR^3} + 8\pi R\sigma = 0 \tag{5b}$$

resulting in a bubble of radius

$$R = \left(\frac{\pi\hbar^2}{16m\sigma}\right)^{1/4} \tag{5c}$$

This model was developed by Tao[8] and by Eldrup et al.[9] employing again the notion of infinite spherical well potential but describing the picked-off electrons as forming a layer of thickness ΔR uniformly coating the inner surface of the bubble. Though such a description has been criticized on account of the unphysical infinite repulsion[12,13] or the unrealistic nature of the sharpness of the bubble edge,[12,13] nevertheless, as a first approximation, the model works rather well in explaining the observations in the case of pure solvents (lifetime and the 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 contractile force of surface tension. As the bubble wall approaches the positronium, bound to the acceptor by some energy $E = -B$ (where B is the binding energy), increasing proximity of the solvent molecules leads (because of the augmented repulsive energy) to a reduction in the binding, until at some radius R_b the Ps-Ac bond is broken, i.e., $B = 0$. Since in the leading approximation the effect of the solvent is represented by an infinite repulsion, this radius R_b depends only on the characteristics of the acceptor and is, in the extreme picture, the same for all solvents. However, we must also consider the fact that the Ps-Ac−bubble system should equilibriate at some radius R_{min} at which the total energy is a minimum, namely,

$$\frac{\partial}{\partial R}[-B + 4\pi R^2\sigma] = 0 \tag{6}$$

Whether the Ps-Ac−bubble system will be stable or unstable will depend on whether R_{min} is greater than or less than the bond breaking radius R_b. In this heuristic picture which is a development based on an important idea which originated with the Moscow group,[14,15] we may proceed to recognize that in the leading approximation R_b is essentially independent of the solvent, while the solvent dependence enters through R_{min}, and that too only through σ. As the surface tension of the solvent is a function of temperature, the equilibrium radius of the bubble, with Ps-Ac within, also depends on temperature, viz., $R_{min}(T) = R_{min}[\sigma(T)]$. As T is decreased, σ increases, and by virtue of eq 6 R_{min} decreases. When R_{min} becomes less than R_b the Ps-Ac−bubble system is no longer stable. Clearly there is a critical value of σ say σ_{cr} at which $R_{min}[\sigma_{cr}] = R_b$ which marks the "water shed" point beyond which the Ps-Ac−bubble system destabilizes. The value of T at which σ becomes σ_{cr} depends on the particular solvent but the value of σ_{cr} does not depend on the solvent (in the first approximation) but only on the acceptor under consideration. We go on to argue that this temperature is, in fact, the turnover temperature, viz., $\sigma(T_0) = \sigma_{cr}$. Indeed at sufficiently high temperature (R) where $\sigma(T) < \sigma_{cr}$ large negative change in enthalpy occurs as the reactant, viz., Ps in the bubble of radius $R = ((\pi\hbar^2)/(16m\sigma))^{1/4}$ reacts with the acceptor and forms the stable Ps-Ac complex in the bubble with radius having shrunk to R_{min}. This makes it a downhill reaction, as for weak acceptors the activation energy is expected to play a sub-dominant role and also the effect of solvent viscosity is negligible as the complex is protected by the bubble from the buffetting of the solvent molecules. It is this negative activation volume that is responsible for the anti-Arrhenius behavior for $T > T_0$. On the other hand for $T < T_0$ when $\sigma(T) > \sigma_{cr}$ the Ps-Ac system in the bubble is unstable, and the formation of the complex takes place in the milieu of the solvent, under constant bombardment by the solvent molecules. This belongs to the Smolochowski regime and following Kramers[16] we may assert that the dependence of the reaction rate on the viscosity (η) goes such as $1/\eta$, and in view of the smallness of the activation energy (for such weak acceptors), we should expect the reaction to be diffusion controlled (noting that the diffusion constant $D \sim 1/\eta$ by virtue of Einstein-Stokes relation). Thus for $T < T_0$ one would expect $\kappa \sim e^{-E}\eta^{/k_BT}$ where E_η is the activation energy associated with the process of diffusion and one observes the typical Arrhenius behavior.

Apart from providing a simplified interpretation of the temperature dependence of the reaction, the model is also able to furnish an explanation of the observed variation with external pressure. 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. However for $T > T_0$ due to the involvement of the bubble a large ΔV^* becomes possible and hence due to the Evans and Polanyi relationship (eq 3) the response to external pressure becomes understandable. Thus the nonmonotonic temperature dependence and the variation with respect to external pressure of the rate get related through this model. If the temperature (T_{expt}) at which the experiment on the variation of the rate with respect to pressure is performed lies above the solvent dependent turnover temperature $(T_0)_s$ then the reaction occurs in the bubble and the rate is susceptible to increase in pressure. If $T_{expt} < (T_0)_s$ then the complex forms in the solution itself and since liquids are essentially incompressible one does not observe significant pressure dependence.

Thus our finding that the turnover region for Ps reaction with nitrobenzene in benzene as a solvent is 33 ± 3 °C and as this lies well above the ambient temperature (T_{expt} = 19 ± 1 °C) at which Kobayashi[4] found no significant pressure dependence of the rate leads support to the model described above as a phenomenon to be expected in the Arrhenius regime. On the other hand, for hexane the ambient temperature is much higher than the turnover region (~ −53 °*C*)[17] and as such the observed significant pressure dependence is quite consistent with the model as the complex is formed inside the bubble.

Furthermore, recognizing that our introduction of the concept of an essentially solvent-independent critical surface tension (characteristic of a given acceptor) has played a critical role in integrating the observed phenomena, we resolve to put this general idea to further experimental verification. Thus we would, on the basis of our model, expect that while the turnover temperature $(T_0)_s$ would vary from solvent to solvent, the values of the surface tension $\sigma_s[(T_0)_s]$ would be a constant for a given acceptor to a first approximation and would equal to σ_{cr}. Accordingly we measured the surface tension of solvents at different temperatures in the relevant range. In the case of nitrobenzene as the acceptor, the turnover point has been estimated by different workers. We have plotted in Figure 4, $\sigma(T)$ as a function of $T - T_0$ for varius solvents. It is gratifying to note that while T_0 differs quite widely from solvent to solvent and values of the surface tension too have quite a substantial spread at a given temperature, nevertheless $\sigma(T_0) = \sigma_{cr}$ for the solvents under consideration lie in a rather small range, namely, 26 ± 2 dynes/cm. It is to be noted that weak attraction of the carbonium ion (C^+) in nitrobenzene and the delocalized π electron cloud of the solvent molecules could be at the root of the small deviation in the case of benzene and toluene. Even though the model is rather simple and somewhat rough and the experimental determination of T_0 for different solvents available through lifetime measurements (determined before 1975) are at best only approximate, it is clear that the picture we have presented above appears to be quite consistent and useful.

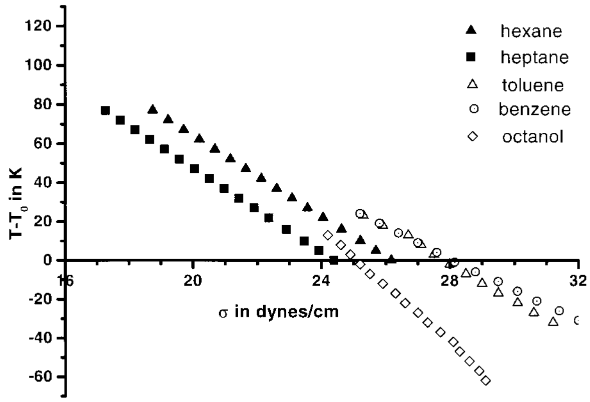

Figure 4. Temperature dependence of surface tension (σ) as measured by us showing the region of critical surface tension (σ_{cr}). (Turnover temperatures T_0 taken from ref 1).

In conclusion, therefore, we have experimentally established that the turnover temperature for Ps−nitrobenzene complex formation in benzene lies in the range 33 ± 3 °C and is thus unambiguously higher than the ambient temperature (T_{expt} = 19 ± 1 °C) at which this reaction was found by Kobayashi[4] to be hardly responsive to external pressure changes. Thus lying as it does in the Arrhenius region it is quite consistent with the heuristic semiquantitative model we have helped develop. The important concept of the existence of a critical surface tension has also been introduced and constitutes a unifying notion for comparing the effects of different solvents for a given acceptor.

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