Physical Chemistry

Corresponding Member of the USSR Academy of Sciences V. I. Gol' danskii, T. A. Solonenko,

1963

SovietRxiv

Abstract

Full Text

Physical Chemistry

Corresponding Member of the USSR Academy of Sciences V. I. Gol' danskii, T. A. Solonenko,
V. P. Shantarovich

QUENCHING OF POSITRONIUM AND INHIBITION OF ITS FORMATION IN AQUEOUS AND ORGANIC SOLUTIONS

Ever since Bell and Graham (^{1}) discovered the presence of two components in the lifetimes of positrons in the condensed phase, observation of the time characteristics of positron annihilation in liquids and solids has been widely used to study the formation of positronium atoms (Ps) and their various interactions. According to the currently accepted view (see, e.g., (^{2})), the component associated with the short lifetime τ_1 (of the order of 10^{-10} sec) is due to annihilation of positrons in the free state and to the decay of para-positronium (^{1}Ps), whereas the long-lived component ($\tau_2 \sim 10^{-9}$ sec) is associated with the formation of ortho-positronium (^{3}Ps) and its subsequent transformations. The fraction of annihilation processes characterized by the positron lifetime τ_2 is usually denoted by I_2.

Since the statistical weights of ortho- and para-positronium are in the ratio 3 : 1, the total probability of positronium formation is evidently equal to $^4/_3\, I_2$.

The influence of various external factors (temperature, pressure, changes in the composition and structure of the substance, etc.) on positron annihilation in the condensed phase can be divided into two main types: 1) quenching of positronium—τ_2 decreases, while I_2 remains unchanged; and 2) inhibition of positronium formation—I_2 decreases at constant τ_2. A combination of both these effects is, of course, also possible.

Quenching of positronium may be explained by the following processes:

a) Conversion of ortho-positronium: $^3S_1 \to {}^1S_0$ on free or unpaired electrons, with formation of the short-lived singlet (para) form.

b) Annihilation of the positron contained in the ^{3}Ps atom on the electrons of other atoms and molecules at the moment of collision of Ps atoms with them (pick-off annihilation).

c) Oxidation-reduction reactions of the type

$$\mathrm{Ps} + \mathrm{Ox} \to e^+ + \mathrm{Red}.$$

d) Addition of Ps atoms to unsaturated molecules, analogous to similar reactions of hydrogen atoms.

As for inhibition of positronium formation, this effect, observed upon addition of NO_3', NO_2' and ClO_4' ions to water (^{3}, ^{4}), was interpreted as a consequence of competition between positronium formation and molecules of the type e^+NO_3. At the same time, however, it remained unclear why an analogous effect of inhibition of positronium formation due to chemical bonds of e^+ with anions was not observed in many other cases (Cl', MnO_4', OH', CH_3COO', etc.).

In principle, there exists another effect that can lead to inhibition of positronium formation. This effect can be explained on the basis of the picture developed by Ore (^{5}) for describing positronium formation in the gas phase. Capture by a positron of an electron from some molecule and formation of positronium occur effectively only when the kinetic energy of the positron T_{e^+} is less than both the ionization potential of the given molecule V and the excitation energy of its first electronic level E. Since the ionization potential of positronium is 6.8 eV, the condition $T_{e^+} > V - 6.8$ eV is also obvious. Consequently, effective formation

positronium occurs in the positron-energy interval $E > T_{e^+} > V - 6.8$ eV (the "Ore gap"), while the probability of its formation P lies within the limits

$$\frac{6.8}{V} > P > \frac{E-(V-6.8)}{E}.$$

It is clear that, when additives are introduced into a solution whose first excitation level is lower than that of the solvent molecules, inhibition of positronium formation can in principle occur. However, such an interpretation cannot be regarded as sufficiently correct for aqueous solutions, where solvation effects are strong—all the more so because, for such inhibitors as NO_3', it is impossible to make a check by determining I_2 for the inhibitor in the pure state.

Therefore, the possibility of describing inhibition of positronium formation in liquids by means of the "Ore gap" should be checked using nonpolar organic solvents as an example.

In the present work we investigated the influence on the main characteristics of the long-lived component—τ_2 and I_2—of additions of NO_3', CrO_4'', Cr_2O_7'', and MnO_4' in aqueous solutions and of additions of C_6H_5J to benzene. For the measurements we used an apparatus (similar to that used in (^{6})), the block diagram of which is shown in Fig. 1. Container 1 with the substance under investigation and with a Na^{22} positron source immersed in it was placed between detectors 2 (scintillation counters with FEU-36 photomultipliers and stilbene crystals). Detector 2a registered the gamma quantum with energy 1.28 MeV, which set the start of the nuclear lifetime time count; detector 2b registered one of the two annihilation quanta with energy 0.5 MeV. Selection of the energies of the registered quanta was carried out using an integral and a differential discriminator.

Fig. 1 block diagram of the apparatus

Figure 1: Fig. 1 block diagram of the apparatus

Fig. 2

Figure 2: Fig. 2

Fig. 1. Block diagram of the apparatus. **1**—sample under investigation, in which the Na^{22} positron source is placed; **2a, b**—scintillation counters; **3**—limiting stages; **K**– "time-amplitude" converter; **CC**—coincidence circuit ($\tau \approx 3 \cdot 10^{-7}$ sec); **ID**—integral discriminator; **DD**—differential discriminator; **AI-100**—one-hundred-channel amplitude analyzer.

The pulses from the FEU anodes were shaped in amplitude and, through a shorted cable, in duration, and were fed to a converter that transformed the time shift of the pulses arriving at its two inputs into amplitude. The amplitude spectrum of the pulses from the converter output was recorded with a one-hundred-channel amplitude analyzer AI-100. The time value of one analyzer channel was $(1.1–1.6) \cdot 10^{-10}$ sec.

Experiments with aqueous solutions showed that the anions CrO_4'', Cr_2O_7'', and MnO_4' cause effective quenching of positronium (a decrease in τ_2), but are not inhibitors of its formation (the value of I_2 is preserved). The form of the curves of the time distribution of positron annihilation in water and in aqueous $K_2Cr_2O_7$ solutions of different concentrations is shown in Fig. 2. The value of τ_2 decreases from $(1.7 \pm 0.1) \cdot 10^{-9}$ sec (water) to $(6.9 \pm 0.6) \cdot 10^{-10}$ sec (0.15 M solution), whereas I_2 remains equal to $18 \pm 2\%$. Similar results were also obtained for CrO_4'' and MnO_4'.

Oxidation of positronium by the MnO_4' anion had already been demonstrated by us earlier (7) from the decrease in the counting rate of 3γ-coincidences. Thus,

···in the present work it has been shown that the action of other oxidizing anions on τ_2 is similar to the action of MnO_4'. The action of NO_3' is entirely different; for it, in our work (using $NaNO_3$ as an example), the results of (3) were confirmed —at unchanged τ_2 the value of I_2 decreased for a 2-5 M solution practically to zero, i.e., complete inhibition of positronium formation was observed.

A very similar picture was also observed by us when iodobenzene was added to benzene, as is seen from Fig. 3.

The values of I_2 for pure benzene and iodobenzene agree with the values given in (8) (35 ± 2% and 4 ± 2%, respectively). At the same time, the values of I_2 obtained in (8) for all halogen derivatives of benzene agree with the lower limits of estimates of the probability of positronium formation in the Ore gap, if the dissociation energy E of the C_6H_5—Hal bonds (9) is taken as the value, as proposed in (9).

Fig. 2. Time-distribution curves of positron annihilation in water (1) and in aqueous solutions of $K_2Cr_2O_7$: 0.005 M (2), 0.015 M (3), 0.025 M (4)

In this connection, the fact we have discovered of sharp inhibition of positronium formation in benzene by even very small additions of iodobenzene ($5 \cdot 10^{-4}$ molecules per one molecule of benzene) becomes of special interest.

In this case there is no longer any basis for ascribing such inhibition to formation of a chemical bond of e^{+} with the C_6H_5J molecule—more effective than could occur for benzene itself. The remaining supposition is that such sharp inhibition is explained by the expenditure of energy of positrons located inside the Ore gap for benzene on excitation of iodobenzene molecules, the cross section of such excitation (σ_{exc}) being approximately 2000 times greater than the cross section, averaged over the Ore gap, for capture by positrons of electrons from benzene molecules (σ_{capt}) with formation of positronium. The upper boundary of the Ore gap for iodobenzene (the bond energy C_6H_5—J) is 2.65 eV (^{10}), i.e., it lies almost at the very lower boundary of the Ore gap for benzene ($V = 9.245$ eV (^{10}), i.e., $V - 6.8 = 2.445$ eV). Therefore the inhibiting action of iodobenzene extends practically over the entire Ore gap for benzene.

For passage through the Ore gap, a positron must undergo about $5 \cdot 10^4$ elastic collisions with benzene molecules. In approximately half of the cases positronium is formed. Consequently, the above-mentioned average capture cross section (σ_{capt}) is about 10^{-5} of the elastic-scattering cross section (σ_y).

The value of σ_y can be estimated on the basis that the entire duration of the positron' s stay in the Ore gap is less than 10^{-10} sec:

$$\frac{5 \cdot 10^4}{n \sigma_y \bar{v}_{e^+}} < 10^{-10},$$

where the concentration of benzene molecules is $n \simeq 6 \cdot 10^{21}$ cm^{-3}, and the average velocity of positrons in the Ore gap is $\bar{v}_{e^+} \simeq 2 \cdot 10^8$ cm/sec. Hence we obtain $\sigma_y > 4 \cdot 10^{-16}$ cm^2 and may take $\sigma_y \approx \sigma_{\text{geom}} \approx 10^{-15}$ cm^2. Using the above-

the above considerations, we then arrive at estimates $\sigma_{\text{capt}} \simeq 10^{-20}$ cm^2 and $\sigma_{\text{excited } C_6H_5J} \simeq 2 \cdot 10^{-17}$ cm^2.

The assumption that the inhibiting effect of small additives on positronium formation in organic solutions can be explained by the ideas of an Ore gap must, of course, be subjected to further experimental verification on a large number of compounds and to detailed quantitative interpretation. At the same time, such an interpretation should lead to a fundamentally new possibility of estimating the energy E of the first excitation levels of a large number of different molecules.

Fig. 3. Curves of the time distribution of positron annihilation in benzene *(1)*,

Fig. 3. Curves of the time distribution of positron annihilation in benzene (1), benzene solutions of iodobenzene: 0.004 M (2), 0.02 M (3), 0.34 M (4), and in iodobenzene (5)

Figure 3: Fig. 3. Curves of the time distribution of positron annihilation in benzene (1), benzene solutions of iodobenzene: 0.004 M (2), 0.02 M (3), 0.34 M (4), and in iodobenzene (5)

benzene solutions of iodobenzene: 0.004 *M* *(2)*, 0.02 *M* *(3)*, 0.34 *M* *(4)*, and in iodobenzene *(5)*.

Meanwhile, such estimates are now acquiring substantial importance, since the energy of the first excitation levels of hydrocarbon molecules is used (11) as a criterion of their radiation stability. It therefore seems expedient to compare the inhibiting action of various additives on positronium formation, which should increase as E decreases, with the radiation yield of radicals from these additives, which in this case, according to (11), should, on the contrary, decrease.

In conclusion, we note that comparison of τ_2 and I_2 for a number of organic compounds gave the following additional results:

1) It was found that τ_2 and I_2 do not change with chain length in the series $C_{nH_{2n+2}}$, where $n = 5$–8 ($\tau_2 \simeq 2.5 \cdot 10^{-9}$ sec.; $I_2 \simeq 30\%$). 2) The lifetime, and in part also the probability of positronium formation, decrease with increasing multiplicity of C–C bonds (example–heptane: $\tau_2 \simeq 2.54 \cdot 10^{-9}$ sec., $I_2 \simeq 30\%$; heptene: $\tau_2 \simeq 2.24 \cdot 10^{-9}$ sec., $I_2 \simeq 30\%$; another example–propyl alcohol: $\tau_2 \simeq 2.3 \cdot 10^{-9}$ sec., $I_2 \simeq 19\%$; propargyl alcohol: $\tau_2 \simeq 1.8 \cdot 10^{-9}$ sec.; $I_2 \simeq 11\%$).

Institute of Chemical Physics
Academy of Sciences of the USSR

Received
8 IV 1963

CITED LITERATURE

1. R. E. Bell, R. L. Graham, *Phys. Rev.*, **90**, 644 (1953).
2. P. R. Wallace, *Advances in Solid State Physics*, **10**, 1 (1960).
3. R. E. Green, R. E. Bell, *Canad. J. Phys.*, **35**, 398 (1957).
4. J. E. Jackson, J. D. McGervey, *Bull. Am. Phys. Soc.*, **7**, 337 (1962).
5. A. Ore, *Univ. Bergen Arb.*, No. 9, 1 (1949).

6. R. E. Green, R. E. Bell, *Nucl. Instrum.*, **3**, 127 (1958).
7. V. I. Gol'danskii, O. A. Karpukhin, G. G. Petrov, *ZhETF*, **39**, 1477 (1960).
8. C. Hatcher, W. Millett, L. Brown, *Phys. Rev.*, **111**, 12 (1958).
9. C. Hatcher, *J. Chem. Phys.*, **35**, 2266 (1961).
10. V. I. Vedeneev, L. V. Gurvich et al., *Handbook: Bond-Dissociation Energies of Chemical Bonds. Ionization Potentials and Electron Affinities*, Publishing House of the USSR Academy of Sciences, 1962.
11. V. V. Voevodskii, Yu. N. Molin, *Radiation Res.*, **17**, 366 (1962).

Note: Figure translations are in progress. See original paper for figures.

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.