Appendix VII

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Positronium Reactions with Diamagnetic

Organic Molecules

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Abstract

Rate constants for the interaction of ortho-positronium atoms with a series of diamagnetic organic compounds have been determined. Nitrated aromatic molecules interact far more readily with ortho-positronium than do nitrated aliphatic molecules. The observed rate constants for the aromatic molecules show a distinct dependency on the nature of the substituents and their relative positions in the aromatic ring. This dependency may be attributed to steric interactions which influence the relative electron charge density on the atoms in the molecule and alter the molecular energy levels.

Introduction

A positron may combine with an electron to form a bound state, positronium (Ps). Positronium can exist in the ground state as para-positronium (an intrinsic lifetime of approximately 10^{-10} sec, with electron and positron spins antiparallel) and ortho-positronium (an intrinsic lifetime of approximately 10^{-7} sec, with electron and positron spins parallel). Annihilation of this ground state results in the production of gamma quanta. By monitoring the gamma emission using delayed coincidence techniques [1,2] lifetime annihilation spectra of positrons and positronium atoms can be obtained. The spectra can normally be resolved into two components, the long-lived ortho-positronium component and a short-lived component that is a combination of para-positronium and free positron annihilations.

Three specific processes may shorten the lifetime of ortho-positronium atoms: ortho-para conversion, "pickoff" and chemical quenching [1]. By a careful choice of the chemical systems reacting with positronium the effects due to chemical quenching can be studied. This paper reports a preliminary study of the quenching interaction on ortho-positronium by various nitrated organic molecules in benzene solution.

Experimental Details

All compounds used were purified by standard techniques, and all samples in benzene solution were degassed by the standard freeze-thaw vacuum technique [3]. The source of positrons was a thin film of $^{22}\text{NaHCO}_3$ evaporated onto a thin aluminum foil immersed in the solutions. Positronium lifetime annihilation spectra were obtained by standard techniques [2].

A bimolecular mechanism was postulated for the organic molecule - ortho-positronium interaction, and this mechanism is derived as follows.

Electron transfer

Complex formation

The rate of disappearance of ortho-positronium is given by:

$$\frac{-d\text{Ps}}{dt} = \text{K}[\text{Ps}][\text{M}]$$

where K is the rate constant for the reaction.

Following integration of this expression and the substitution when $t=0$,

$[\text{Ps}] = [\text{Ps}]_0$ gives

$$\frac{-\ln[\text{Ps}]}{t} = \frac{-\ln[\text{Ps}]_0}{t} + \text{K}[\text{M}]$$

which can be expressed as:

$$\lambda_2 = \lambda_0 + \text{K}[\text{M}].$$

λ_2 is the annihilation rate of ortho-positronium for a given concentration [M] of the organic molecule in a solvent (benzene), and λ_0 is the annihilation rate of ortho-positronium in the pure solvent. By varying the concentration of the organic reactant and measuring the variation in the annihilation rate of ortho-positronium (the absolute gradient of the ortho-positronium component in the lifetime spectra) a rate constant for the reaction can be obtained. Examples of the data for the nitrotoluenes in benzene are given in Fig. 1. All rate constants were calculated using a linear least-squares program.

Results and Discussion

Rate constants for the interaction of ortho-positronium are given in Tables 1 and 2. SCF molecular orbital calculations (INDO) were made to determine various molecular reactivity parameters of the unperturbed reactant molecules [4]. The energies of the lowest unoccupied molecular orbital (LUMO) and the net π -charge density on the carbon atoms of the substituted ring system obtained from these calculations are also listed in Table 1. Co-planar models were used, except for the ortho derivatives in which a $-\text{NO}_2$ group was rotated from 0 to 90° out of

the plane of the aromatic ring in increments of 30° .

The dinitrobenzenes, nitrotoluenes and chloronitrobenzene data have one obvious similarity: the ortho derivative has lower rate constant than its meta and para analogs. This can be related to the electron delocalization in these molecules, and the consequences of steric interaction inhibiting this delocalization in the ortho derivatives. The meta and para derivatives contain $-\text{NO}_2$ groups that are assumed to be co-planar with the aromatic ring, and electron charge is removed from the ring system by the electronegative oxygen atoms. In the ortho derivatives steric interaction between the two substituents is strong, forcing a $-\text{NO}_2$ group out of the co-planar position and inhibiting electron delocalization onto the oxygen atoms. Another ortho effect of importance is the increase in the energy of the LUMO. Postulating an electron transfer mechanism, the higher the energy of the LUMO, as in the case of the ortho derivative, the lower should be the rate constant.

The rate constant data reflects further effects. The dinitrobenzene compounds react more readily than the mono nitro compounds because two nitro groups are involved in the delocalization of the π -charge. The relative rate constants for the meta and para derivatives of nitrotoluene and chloronitrobenzene can be attributed to the inductive effect of the methyl group and the mesomeric effect of the chlorine group, respectively [5]. The strong electron donating effect of the $-\text{NH}_2$ group in the nitroanilines dominates over the electron withdrawing ability of the $-\text{NO}_2$ group, hence all three derivatives have excess negative charge in the π -ring system. It should also be noted that the energy of the LUMO for the nitroanilines correlates with the observed rate constants, lending more credibility to the electron transfer mechanism. The energy levels of the LUMOs for the nitroalkanes are higher than those of the aromatic systems, and no rapid quenching is observed (Table 2). Ortho-positronium in the pure

nitroalkanes has a measurable lifetime, and rate constants are typically lower by a factor of 10^3 . The nitro group alone does not rapidly quench ortho-positronium.

Summary

Extending the correlations mentioned above to more general positronium interactions proves to be more difficult. Thus anthracene which has a low energy LUMO does not rapidly quench ortho-positronium. Rather it is a subtle combination of the aromatic system and the chemical nature of the substituent groups which rapidly quenches the ortho-positronium component in a lifetime annihilation spectrum. By a specific choice of chemical systems for study an attempt can be made to resolve the nature and the mechanism (specific reaction sites) for the quenching of ortho-positronium by organic molecules.

Table 1

Compound	Rate constant (± 0.2) ($K \times 10^{-10} \text{ M}^{-1} \text{ s}^{-1}$)	$\theta^\ddagger$	Energy (ev) LUMO	Σq_i^*
Nitrobenzene	2.7	0	3.883	0.0236
1,2-dinitrobenzene	3.3	0 30 60 90	3.143 2.724 2.915 3.072	0.0388 0.0170 0.0055 -0.0025
1,3-dinitrobenzene	4.7	0	2.956	0.0408
1,4-dinitrobenzene	5.0	0	2.319	0.0364
2-nitrotoluene	0.85(± 0.20)	0 30 60 90	3.817 4.002 4.598 5.114	0.0195 0.0085 -0.0111 -0.0217
3-nitrotoluene	2.1	0	3.888	0.0217
4-nitrotoluene	2.2	0	3.709	0.0220
1-chloro 2-nitrobenzene [†]	2.5	-	-	-
1-chloro 3-nitrobenzene [†]	3.5	-	-	-
1-chloro 4-nitrobenzene [†]	3.1	-	-	-
2-nitroaniline	1.0	0 30 60 90	4.1873 4.3830 4.9214 5.2740	-0.1179 -0.1268 -0.1461 -0.1567
3-nitroaniline	1.9	0	3.9915	-0.1197
4-nitroaniline	0.5(± 0.06)	0	4.4864	-0.1137

[‡] θ Angle of rotation in degrees of one $-\text{NO}_2$ group relative to the ring system

* Σq_i Net π -charge density on the carbon atoms of the substituted ring system

[†] The SCF closed shell program calculations are only valid for molecules containing hydrogen through to fluorine.

Table 2

Compound	Rate constant ($K \times 10^{-7} \text{ M}^{-1} \text{ s}^{-1}$)	Energy (eV) LUMO
nitromethane	1.70(± 0.30)	4.3667
nitroethane	2.05(± 0.20)	4.4945
1-nitropropane	2.19(± 0.15)	4.5706
2-nitropropane	1.84(± 0.15)	4.5190

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Fig.1 The Annihilation Rate (λ_2) of ortho-positronium Plotted

Against the Concentration of the Nitrotoluenes in Benzene.

Figure 1: The Annihilation Rate (λ_2) of ortho-positronium Plotted
Against the Concentration of the Nitrotoluenes in Benzene

Table 1: Rate constant data for the interaction of ortho-positronium with
nitroated aromatic compounds, and related molecular parameters
--concentration range of approximately 0 to 30 millimolar.

Table 2: Rate constant data for the interaction of ortho-positronium with
nitroalkanes, and related molecular parameters. --concentration
range of approximately 0 to 15 molar.