

# Reactivity of some S-bridge containing diphenyl derivatives (sulfides, sulfoxides, sulfones) towards *ortho*-positronium atoms in dimethylsulfoxide solution

Béla Lévy<sup>a,\*</sup>, Dénes Szabó<sup>b</sup>

<sup>a</sup> Department of Nuclear Chemistry, Eötvös Loránd University, Budapest, Hungary

<sup>b</sup> Department of Organic Chemistry, Eötvös Loránd University, Budapest, Hungary

Received 10 January 2006; accepted 6 March 2006

Available online 10 March 2006

## Abstract

The effect of changes in the chemical structure of organic sulfur compounds on their reactivity towards an *ortho*-positronium (*o*-Ps) atom was investigated by positron annihilation lifetime spectroscopy in dimethylsulfoxide solutions. S-bridge containing molecules with very similar structural frameworks were selected as model systems, such as, diphenyl sulfide, sulfoxide and sulfone, and their derivatives. The effect of the type of the S-bridge on the reactivity increased in the order of S < SO < SO<sub>2</sub> in all groups of the compounds with similar substituents on their phenyl groups. The same trend was observed for the calculated excess positive charge on the sulfur atoms and the LUMO energies of the molecules too. As it was expected, electron-withdrawing substituents on the aromatic rings increased both the reactivity and the negative values of the LUMO energy of the molecules (COOH < NO<sub>2</sub>) whereas those with electron-donating character (CH<sub>3</sub>O) showed the opposite effect.

© 2006 Elsevier B.V. All rights reserved.

**Keywords:** Positron annihilation; Lifetime spectroscopy; S-bridge containing diphenyl derivatives; Substituent effects; Reaction rate constants; Activation parameters

## 1. Introduction

A positronium (Ps) atom is the bound state of an electron (e<sup>-</sup>) with its antiparticle a positron (e<sup>+</sup>) [1–3]. It is the simplest hydrogen like exotic atom, the lightest, “0 mass number isotope” of hydrogen. As a chemical species, it is the simplest radical, and as such, it is very reactive, having a nucleophilic character. Through its different decay modes into  $\gamma$  quanta (annihilation) it can be used as a labeled atom and it has proved to be an efficient microprobe of various physical and chemical properties of matter.

A Ps atom may be formed when an energetic positron originating from a radioactive decay enters a condensed

medium. It will thermalize within a few picoseconds by losing its kinetic energy via ionization of the molecules of the medium. According to the basic idea of the spur model of positronium formation [4] a thermalized positron can form a Ps atom with an electron which is freed by the positron itself in its ionization track or spur. Due to the different spin combinations of a positron and an electron, there are two possible Ps states, the *para*-Ps (*p*-Ps) with antiparallel (singlet) spin state and *ortho*-Ps (*o*-Ps) with parallel (triplet) spin state. The intrinsic lifetimes of *p*-Ps and *o*-Ps are 0.125 and 140 ns, respectively.

Positron annihilation lifetime spectroscopy is the experimental technique which can provide information on the mean lifetimes ( $\tau_i$ ) or decay rate constants ( $\lambda_i = 1/\tau_i$ ) and the relative yields or intensities ( $I_i$ ) of the different positron states in the given medium. For systems in which positronium formation occurs the lifetime spectra can generally

\* Corresponding author. Fax: +361 372 2608.

E-mail address: [levay@para.chem.elte.hu](mailto:levay@para.chem.elte.hu) (B. Lévy).

be analyzed in terms of three exponential components, assigned to three distinct positron states. In increasing order of lifetime values, these are the *p*-Ps ( $\tau_1$ ), the free positrons ( $\tau_2$ ) and the *o*-Ps ( $\tau_3$ ), respectively.

In condensed medium the long lifetime of *o*-Ps is shortened down to a few nanoseconds due to the so-called pick-off annihilation, whereby the positron in the *o*-Ps atom seeks out an electron in the surrounding molecules with opposite spin and annihilates with it instead of its own electron. No special chemical interactions between *o*-Ps atom and the surrounding medium are involved in this process.

On the other hand, if the *o*-Ps atom takes part in chemical reactions (e.g., substitution, oxidation, complex formation, etc.) with certain molecules of the system, its annihilation characteristics will depend strongly on the physical and the chemical structure of these molecules. In solution the chemical interactions (due to the increased proximity of electrons with opposite spin) will shorten the mean *o*-Ps lifetime as compared to the characteristic pick-off lifetime of the pure solvent. These processes are called “quenching” of *o*-Ps.

Certain groups of compounds such as diamagnetic nitro-aromatics, conjugated compounds such as maleic anhydride and quinones, containing highly electronegative N and O heteroatoms and nitriles, have proved to be very effective *o*-Ps quenchers [5–7]. All these molecules are known as good electron acceptors and *o*-Ps reacts with them via donor–acceptor interaction [8]. Clear correlation was found between the reactivity of substituted nitrobenzenes and the Hammett’s  $\sigma$  constant of the corresponding substituents [8]. It was shown that the positively charged carbon atoms of the molecules are the reactive centers where the nucleophilic *o*-Ps attacks the molecule [5,9,10].

In our previous papers [10–13] we showed that positron annihilation lifetime spectroscopy can provide information also on subtle structural changes in the molecules, if an appropriate model system is selected and the comparison is based on a series of molecules with a common structural framework.

Unfortunately, practically no positron annihilation lifetime data are available for organic sulfur compounds in the literature. According to our best knowledge, only a single old paper of Goldanskii et al. [14] discusses the changes in the reactivity of a molecule towards *o*-Ps atom caused by the inserting of a sulfur bridge into it (Table 1).

The authors of Ref. [14] interpret the data of Table 1 as follows. The substitution of an electron donating NH<sub>2</sub> group onto the nitrobenzene molecule in *para* position to

the NO<sub>2</sub> group strongly compensates the electron withdrawing effect of the latter. Hence, because of the decreased electron deficiency of the aromatic ring, the reactivity of the molecule towards the *o*-Ps atom drastically decreases. The electron transfer between the electron donating and electron withdrawing substituent groups in the *p*-nitro-aniline molecule is easy because they are separated by a conjugated bond system of good electron conducting property. If, however, an S-bridge of much lower conductance is inserted between the NH<sub>2</sub> and NO<sub>2</sub> groups the compensation effect of the NH<sub>2</sub> group becomes much weaker and the reactivity of the molecule, as compared to the nitrobenzene, decreases much less than without the presence of the S-bridge.

In our opinion, however, the above explanation for the change caused in the reactivity of a molecule by inserting a sulfur or other type of bridge into it is quite simplified. It seems difficult to characterize the effect of a bridge quantitatively or to correlate it with quantitatively measurable molecular properties.

The aim of the present work was to use positron annihilation lifetime spectroscopy to determine the relevant factors responsible for the differences in the reactivity of a series of S-bridge containing organic molecules (sulfides, sulfoxides, sulfones) with similar structural framework towards the nucleophilic *o*-Ps atom. It is also of interest to compare the positronium chemistry results with the chemistry of sulfides, sulfoxides and sulfones [15] and with the nature of the different types of the sulfur bonding [16].

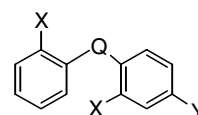
As a model system for this twofold aim, S-bridge containing diphenyl derivatives (**1–3 a–d** in Fig. 1) were selected.

## 2. Experimental section

### 2.1. The preparation of the S-bridge containing compounds

Diphenyl sulfide (**1a**), diphenyl sulfoxide (**2a**) and diphenyl sulfon (**3a**) were purchased from Sigma–Aldrich. The syntheses of sulfides **1b**, **1c** and **1d** have been published previously [17]. The preparation of sulfoxides **2b**, **2c**, **2d** and sulfone **3b** has also been described [18,19].

*2-Carboxy-4-methoxyphenyl 2-carboxyphenyl sulfone* (**3c**). To the solution of sulfide **1c** (0.9 g, 2.9 mmol) in



**1:** Q = S; **2:** Q = SO; **3:** Q = SO<sub>2</sub>

**a:** X = Y = H  
**b:** X = COOH, Y = H  
**c:** X = COOH, Y = CH<sub>3</sub>O  
**d:** X = COOH, Y = NO<sub>2</sub>

Fig. 1. The investigated S-bridge containing compounds.

Table 1  
Effect of the inserting of a sulfur bridge into the *p*-nitro-aniline molecule on its reactivity towards *o*-Ps atom

compound	$k_s$ (M <sup>-1</sup> s <sup>-1</sup> )
H–C <sub>6</sub> H <sub>4</sub> –NO <sub>2</sub>	$1.1 \times 10^{10}$
H <sub>2</sub> N–C <sub>6</sub> H <sub>4</sub> –NO <sub>2</sub>	$1.0 \times 10^8$
H <sub>2</sub> N–C <sub>6</sub> H <sub>4</sub> –S–C <sub>6</sub> H <sub>4</sub> –NO <sub>2</sub>	$2.8 \times 10^9$

Download English Version:

<https://daneshyari.com/en/article/5376856>

Download Persian Version:

<https://daneshyari.com/article/5376856>

[Daneshyari.com](https://daneshyari.com)