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Appendix IV
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A Study of the Electron Donor-Acceptor Properties of Diamagnetic
Organic Molecules Via Positronium Reactions.¹

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Positrons, generated by the radioactive decay of certain nuclides, may, while losing their kinetic energy in collisions with surrounding molecules, combine with an electron to form an electron-positron bound state, the positronium atom (Ps).² This species has a lifetime of about 10^{-7} to 10^{-10} s which is too short for its reactions to be followed by conventional product analysis. The chemical reactions of positronium can be studied by observing changes in its average lifetime and decay modes which are dependent on the chemical reactivity and physical composition of its environment. This feature, as well as the simplicity of the species, makes the positronium atom a useful probe for the assessment of molecular properties via kinetic measurements.

The annihilation of positronium in simple organic solvents has been comprehensively studied³, and the effects following the addition of diamagnetic species have been observed.⁴⁻⁶ In the following, we should like to report the results of a preliminary study of the interactions of positronium with nitrobenzene and ortho, meta and para derivatives of nitrotoluene and dinitrobenzene in benzene solutions. Distinct differences in the rate constants for the reaction of positronium with the organic molecules were observed for the various systems, and an attempt was made to correlate these changes to certain molecular parameters and to the effects of steric interactions in these molecules.

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All compounds were purified by standard techniques. The ^{22}Na positron source consisted of a thin film of carrier free $^{22}\text{NaHCO}_3$ evaporated on to an aluminum foil (1 mil. thick) immersed in the organic solution. The sample was thoroughly degassed using a simple vacuum-freeze-thaw technique to remove all dissolved oxygen. Positronium annihilation spectra were obtained by standard techniques.⁷ By varying the millimolar concentration of the nitrated compounds dissolved in benzene, rate constants for the interactions of ortho positronium in the various solutions were obtained and are given in the table. These values show that the rate of the reaction is dependent upon the number of nitro groups attached to the solute ring system, and whether these nitro groups are planar to and can delocalize with the ring Π electrons.

The differences in the rate constants for positronium reactions of ortho-nitrotoluene compared with meta and para-nitrotoluene, and ortho-dinitrobenzene compared with meta and para-dinitrobenzene, can be explained in terms of electron delocalization in these systems⁸, and the consequences of steric interaction inhibiting this delocalization in ortho-nitrotoluene and ortho-dinitrobenzene. In the meta and para derivatives, the $-\text{NO}_2$ groups are co-planar with the aromatic carbon 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 of the ring is strong, forcing a $-\text{NO}_2$ group out of the co-planar position necessary for maximum Π orbital overlap. Electron delocalization out of the ring to the oxygen atoms is inhibited. The induced positive nature of the ring system for the meta and para derivatives seems to result in faster reactions with positronium than for the equivalent ortho derivative. The dinitrobenzene compounds react more readily because two nitro groups are involved in the delocalization of the Π -charge, and the smaller rate constants for meta and para-nitrotoluene compared with that of nitrobenzene can be attributed to the inductive effect

of the methyl group. From this initial study it can be seen that positronium annihilation studies are reflecting the geometry of the quenching molecules.

The extended Hückel self-consistent field molecular orbital theory with intermediate neglect of differential overlap⁹ has been used to calculate the magnitudes of delocalization effects and other reactivity parameters (e.g. free valence, the energies of the HOMO and LUMO) in these molecules. 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 ring's axis in increments of 30° . Some of the molecular parameters showing a correlation with the rate constant data are listed in the table. The energies of the lowest unoccupied molecular orbitals (LUMO), and the net π charge density on the carbon atoms of the substituted ring system are listed. As the energy of the LUMO increases and the net π electron density on the benzene ring carbon atoms decreases, the rate of positronium reaction decreases. Free valence, the energy differences between LUMO and HOMO, and the net $(\pi + \sigma)$ electron charge densities showed no discernible correlation with the rate constant data.

The calculated data suggest that the mechanism for the quenching of ortho-positronium atoms is that of a thermalized positronium atom reacting with the substrate molecule by electron donation to the lowest unoccupied molecular orbital. The relative ease of this electron transfer process is reflected by the magnitude of the rate constants.

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Table rate constant data for the quenching of ortho-positronium
and related molecular parameters

Compound	Rate constant $k \times 10^{-10} \text{ M}^{-1} \text{ s}^{-1}$ (± 0.2)	$\theta^\ddagger$	Energy (eV)	Σq_H^*
			LUMO	
Nitrobenzene	2.7	0	3.883	0.0236
o-dinitrobenzene	3.2	0	3.143	0.0388
		30	2.724	0.0170
		60	2.915	0.0055
		90	3.072	-0.0025
m-dinitrobenzene	4.7	0	2.956	0.0408
p-dinitrobenzene	5.0	0	2.319	0.0364
o-nitrotoluene	0.85	0	3.817	0.0195
		30	4.002	0.0085
		60	4.508	-0.0111
		90	5.114	-0.0217
m-nitrotoluene	2.1	0	3.888	0.0217
p-nitrotoluene	2.2	0	3.709	0.0220

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

* Σq_H Net Π charge density on the carbon atoms of the substituted ring systems