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Molecular Complex Formation between Positronium and Organic Molecules in Solutions[1]

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Abstract: Evidence is presented which supports the reversible formation of molecular complexes between Ps atoms and a series of nitrobenzene derivatives and *p*-benzoquinone in solution. The activation energy for the forward reaction step I (Ps + M (II) $\rightleftharpoons$ PsM (I)) is generally very small. $E_A \sim 1$ kcal/mol. ΔH_{EQ}, the enthalpy of the overall process, ranges from almost zero, in the case of very unreactive substrates, such as toluene or heptane, to −8 kcal/mol for dinitrobenzene or *p*-benzoquinone. The reactivities of the various substrate molecules toward Ps follow trends as observed in conventional molecular complex formation. Furthermore an attempt has been made to assess the role of the solvent upon the stability of the molecular complexes.

Positrons which are generated as the result of the radioactive decay of neutron deficient nuclides with initially several hundred kiloelectron volts of kinetic energy lose their energy in elastic and inelastic collisions with the surrounding matter until they become thermalized or nearly thermalized. At this point the probability for the annihilation as "free" positrons by two-photon decay assumes a maximum value.[2] During the slowing down process the positrons pass through an energy region (Ore gap) where the translationally excited positron can abstract an electron from surrounding matter and form the bound state of positronium (Ps). Ps exists in two ground states The singlet (para) Ps with antiparallel spin orientation (↑↓) has a self-annihilation lifetime in free space of 1.25×10^{-10} sec and it decays by two-photon emission. The triplet (ortho) Ps with parallel spin orientation (↑↑) has a considerably longer intrinsic lifetime of 1.4×10^{-7} sec. Its self-annihilation occurs via three-photon emission. Ortho and para Ps are normally formed in the ratio 3:1. These Ps atoms are generated in accordance with the Ore model with kinetic energies ranging from 6.8 eV down to thermal energies. Thus it seems quite feasible that a certain fraction of them may undergo chemical reactions while still possessing appreciable amounts of kinetic energies whereas other Ps atoms may become thermalized before they react.

In condensed matter, such as in solutions, the thermalization time of Ps is of the order of 0.7 nsec (Figure 1).[2d] Thus, the presence of the thermalized Ps can be recognized by the appearance of a second (long lived) component in the lifetime time spectra. Thermal Ps interaction with matter, which leads to an enhanced annihilation of the positron (bound in the Ps), results in characteristic changes of the average lifetime, τ_2, associated with this long-lived component.

On the other hand the lifetime of the positrons incorporated in positronium atoms taking part in "hot" reactions (Figure 1) is indistinguishable from that of the free positrons or *p*-Ps, which have a considerably shorter lifetime in condensed matter and appear as a part of the short-lived component.

Recent studies[2] have shown drastic differences in the reactivity of thermal Ps atoms toward various categories of chemical compounds. The first group which is relatively unreactive toward Ps comprises, among others, the aliphatic and aromatic hydrocarbons, alcohols, halogenated hydrocarbons, aliphatic nitro compounds,[3-5] phthalic anhydride,[6] and (diamagnetic) inorganic ions in aqueous solution having a standard redox potential $E_0 < -0.9$ eV. This is in sharp contrast to a second category of molecules, such as nitroaromatics,[7-11] quinones,[12] maleic anhydride, tetracyanoethylene,[6] halogens,[13] carbonium ions,[14] and certain inorganic ions in solutions,[8,15-22] the latter having a standard redox potential of $E_0 > -0.9$ eV, which react very rapidly with Ps atoms.

In the case of the inorganic (or organic) ions present evidence based on the existing correlation between the oxidizing capabilities of the ions and the observed reactivity allows a satisfactory interpretation in terms of an electron transfer from Ps to the ion when energetically possible.[18-20] No such obvious relationship seems to exist between the measured Ps reaction rates and the reported electron affinities of various groups of diamagnetic organic molecules.

Thus in the following the reactions of a number of diamagnetic organic molecules, which exhibit a high reactivity toward Ps, were investigated in greater depth to elucidate the reaction mechanisms involved and the parameters which control the reaction.

Monosubstituted nitrobenzene derivatives have been used

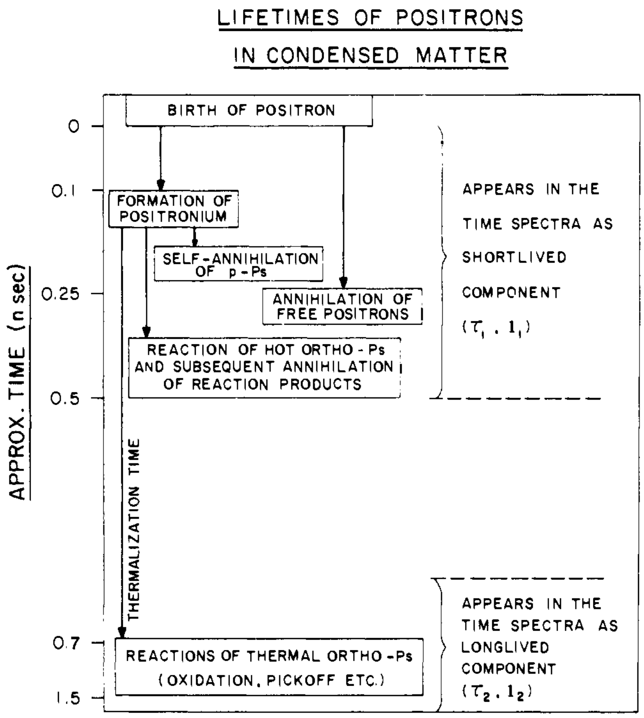

Figure 1. Time scale for the progress of the various types of interactions between e$^+$ or Ps and solute or solvent species in solution.

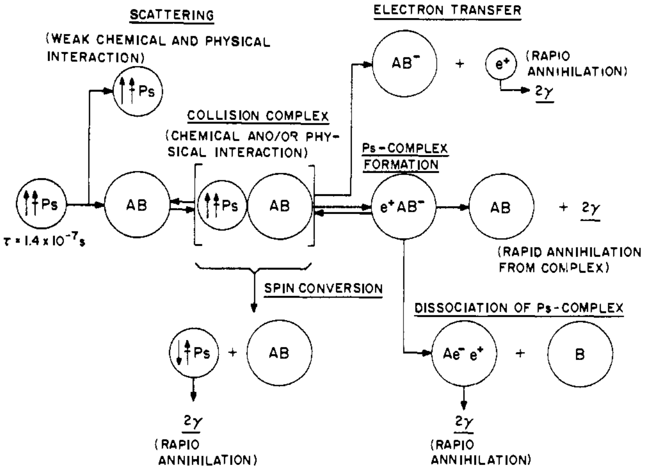

Figure 2. Schematic representation of possible o-Ps interactions with matter.

to study the steric nature of the ortho effect, and satisfactory correlation has been made between the rates for positronium reactions with meta and para derivatives and the Hammett parameters characteristic of the second nitrobenzene substituent. The data support the idea of stereospecificity, the reactions obeying the same chemical reactivity correlations as those found for classical, general chemical reactions.

From the temperature dependence of the reaction rate constants observed in this study it is evident that Ps atoms form more or less stable complexes with the reactant. It appears that the observed behavior can at least semiquantitatively be interpreted in terms of the electron donor-acceptor or molecular complex theory.[23]

Because of the simplicity of the species involved it seems that the reactions of the Ps atom offer a unique opportunity for the study of the electron acceptor properties of organic molecules. This could include an assessment of their electron affinity in solution, and an evaluation of the role which the solvent may play in the stabilization of the resulting molecular complexes.

Experimental Section

(a) Positron Lifetime Measurements. The positron emitter used is ^{22}Na, which decays under emission of a positron to the excited state of ^{22}Ne, which in turn undergoes deexcitation under emission of a 1.27 MeV photon. The lifetime of the excited ^{22}Ne is only 3 psec, so that for all practical purposes the emission of the positron and 1.27 MeV photon can be considered to occur simultaneously. Thus the positron lifetime distribution can be determined by observing the time elapsed between the generation of the 1.27 MeV photon and the appearance of the 0.51 MeV photons resulting from the annihilation of the positron. These timing measurements have been carried out by conventional fast-slow coincidence techniques as previously described.[24]

(b) Purity and Source of Reagents. All solvents were of highest available purity (Phillips Research Grade) and when necessary they were dried by means of a molecular sieve and redistilled.

The other compounds used in this investigation were obtained from different sources. They were purified by suitable methods, distillation, recrystallization, and preparative gas chromatography, until subsequent tests showed a purity of better than 99.5%.

(c) Preparation of Samples. Specially designed sample vials (cylindrical glass tubes 100 mm long and 10 mm i.d.) were filled with 1 ml of sample solution. The positron sources were 3-5 μCi ^{22}Na, prepared by evaporating carrier free neutral solutions of either ^{22}NaHCO$_3$ or ^{22}NaCl (obtained from ICN) onto a thin aluminum foil. The radioactive foils were suspended in the solutions, and all solutions were carefully degassed by freeze-thaw techniques to remove oxygen. When necessary as in the temperature studies the vials were sealed off and immersed in a specially designed thermostat which controlled the temperature within ±1.0°. For the low-temperature work the sample vial was immersed in suitable cooling mixtures in a specially designed dewar vessel.

Special care has been taken to evaluate the potential effects of heat and irradiation (by the ^{22}Na source) on the substrate compound and source support. Thus in all temperature studies the following procedure was followed. Data points were first obtained at increasing temperatures. After carrying out the high temperature measurements the cycle was reversed and data were obtained at decreasing temperatures. The fact that the data were found reproducible throughout the full cycle clearly indicated that no significant changes occurred in the solution or in the aluminum foil.

Results and Discussion

(a) General Aspects of Thermal o-Ps Atom Reactions. Quantum mechanics[2] predicts that the annihilation lifetime of the positron is basically determined by the degree of overlapping of positron and electron wave functions, which leads, e.g., to the intrinsic lifetime of o-Ps of 1.4 × 10^{-7} sec. Starting from this general principle the following conclusions can be drawn as to the fate of the o-Ps in a solution if solvent effects are provisionally neglected.

In a collision between o-Ps and another molecule a more or less long-lived collision complex may be formed, in which the electron density at the position of the positron will be drastically increased, Figure 2. The average time that the Ps spends in this complex will depend on the stability of this complex. If only weak (van der Waals) forces are operative in holding this complex together, the Ps will spend only very little time in this environment, the positron experiences only for a short time the effect of the increased electron density, and the average lifetime of the Ps appears only slightly shorter compared with the intrinsic lifetime of the o-Ps. On the other hand if this Ps collision complex undergoes stabilization involving stronger intermolecular forces, or genuine chemical bond formation, then the positron will find itself for a prolonged period in an environment of high electron density, and its lifetime will be substantially reduced. In other cases this complex may be just a transition state leading to electron transfer from Ps to substrate (oxidation of Ps). The product of this latter process is a free positron, whose lifetime in condensed matter is considerably shorter[2] (0.1–0.5 nsec) than that of the *o*-Ps. If the substrate is paramagnetic the collision can result in a spin conversion from *o*- to *p*-Ps, whose intrinsic lifetime is only 1.25×10^{-10} sec.[2] (Because of the extremely short intrinsic lifetime of the *p*-Ps, reactions of this species can be neglected.) Thus, one can generally state that all interactions of the *o*-Ps with matter lead to a shortening of its apparent lifetime.

In order to obtain an accurate determination of the reactivity of thermal Ps toward various substrates one has to develop these qualitative predictions to a quantitative method for the calculation of the chemical rate constants for the reactions between Ps and substrate.

Consistent with this general concept the following reaction scheme has been applied to assess the reactions of thermal Ps in a dilute solution of a *diamagnetic* substrate (M).

$$2\gamma \xleftarrow[\lambda_p]{\text{annihilation in solvent}} \text{Ps} + \text{M} \underset{K_2}{\overset{K_1}{\rightleftharpoons}} \text{PsM} \xrightarrow{\lambda_c} 2\gamma \text{ annihilation} \quad (1)$$

According to the above reaction scheme[24] the following reactions have been considered. 1. Reaction of Ps with substrate M to form a Ps complex PsM (rate constant K_1). (If the chemical reaction is the oxidation of Ps, it is assumed that the reaction occurs via the complex PsM and that the subsequent electron transfer is fast; i.e., complex formation is considered to be the rate-determining step.) 2. Decomposition of PsM (rate constant K_2). 3. Positron annihilation in complex (decay constant λ_c). 4. Annihilation of Ps in bulk solvent with rate λ_p.

Since the concentration of M remains essentially constant throughout the experiment the mechanism can be simplified to

$$2\gamma \xleftarrow{\lambda_p} \text{Ps} \underset{K_2}{\overset{K_1'}{\rightleftharpoons}} \text{PsM} \xrightarrow{\lambda_c} 2\gamma \quad (2)$$

$$K_1' = K_1[\text{M}]$$

$$\mathrm{d}[\text{Ps}]/\mathrm{d}t = -(K_1' + \lambda_p)[\text{Ps}] + K_2[\text{PsM}] \quad (3)$$

$$\mathrm{d}[\text{PsM}]/\mathrm{d}t = K_1'[\text{Ps}] - (K_2 + \lambda_c)[\text{PsM}] \quad (4)$$

and appropriate kinetic equations can be set up. By integrating the resulting differential equations, the population of the various states in which the positrons exist, *o*-Ps and PsM, can be found as a function of time. From these value and the positron annihilation constants for these states, the time-dependent two-photon annihilation rate $R_{2\gamma}$ can be calculated.[2] It is represented by the following two-exponential equation

$$R_{2\gamma} = A \exp(-\lambda_1 t) + B \exp(-\lambda_2 t) \quad (5)$$

A and *B* are scaling factors, related to the number of positrons annihilating at a rate λ_1 or λ_2.

λ_1 is a composite of the annihilation rates for free positrons, self-annihilation of *p*-Ps and includes the annihilation rates of positron compounds formed as a result of "hot" Ps reactions.[19]

Under the experimental conditions in this study, where the concentration of the substrate, [M], is in the millimolar range, the following inequality can be assumed: $(K_2 + \lambda_c) \gg K_1[\text{M}]$.[26] λ_2 is then given by the following expression

$$\lambda_2 = \lambda_p + \frac{K_1\lambda_c}{K_2 + \lambda_c}[\text{M}] \quad (6)$$

$$K_1\lambda_c/(K_2 + \lambda_c) = K_{\text{obsd}}$$

Table I. Examples of Chemical Compounds Showing Strong/Weak Interactions with Positronium[a]

Strong interaction $k_{\text{obsd}} > 10^8\ M^{-1}\ \text{sec}^{-1}$	Weak interaction $k_{\text{obsd}} < 10^8\ M^{-1}\ \text{sec}^{-1}$
Nitroaromatics. quninones. maleic anhydride, tetracyanoethylene, halogens, inorganic ions in solution ($E_\circ > -0.9$ eV), organic ions in solution	Simple aliphatic or aromatic hydrocarbons: alkanes, benzene. anthracene, etc.. aniline. phenol, haloalkanes, halobenzenes, aliphatic nitro compounds. phthalic anhydride. benzonitrile, (diamagnetic) inorganic ions in solution ($E_\circ < -0.9$ eV)

[a] Data measured in this study are in general agreement with those reported previously, ref 3–22.

or if

$$\lambda_c \gg K_2 \text{ then } \lambda_2 = \lambda_p + K_1[\text{M}] \quad (7)$$

By determining λ_p which is identical (in dilute solutions) with λ_2 measured in the pure solvent and knowing the solute concentration, [M], the apparent constant for Ps reaction is given by

$$K_{\text{obsd}} = \frac{\lambda_2 - \lambda_p}{[\text{M}]} \quad (8)$$

The K_{obsd} quoted are the average values obtained from at least 9–10 lifetime measurements taken at different solute concentrations [M].

λ_2 is the slope of the long-lived component in the time spectrum and can be accurately obtained by computer analysis.

(Since λ_2 as well as λ_p are temperature dependent, both types of experiments have to be carried out under identical conditions.)

(b) Reactivity of Thermal Ps Atoms toward Nitroaromatics (Correlation with Hammett's Constants and the Ortho Effect). In the first series of experiments the reactivity of a number of diamagnetic compounds toward Ps was measured by the technique described above. The results which generally agree with those reported by other authors show that these compounds can be generally divided into two categories (Table I). The first one which shows only weak interaction with Ps ($K_{\text{obsd}} < 10^8\ M^{-1}\ \text{sec}^{-1}$) is composed of hydrocarbons, halogenated hydrocarbons, aliphatic nitro compounds, and diamagnetic inorganic ions, whose standard redox potentials in aqueous solution are more negative than −0.9 eV. The second group encompasses nitroaromatics, quinones, halogens, conjugated anhydrides, tetracyanoethylene, organic ions, and inorganic ions with a standard redox potential of greater than −0.9 eV and displays a strong reactivity toward Ps ($K_{\text{obsd}} > 10^8\ M^{-1}\ \text{sec}^{-1}$).

Perhaps the simplest explanation for this behavior, at least so far as the neutral molecules are concerned, can be provided by discussing the results semiquantitatively in terms of the electron donor–acceptor or molecular complex theory.[23] According to this model the intermolecular binding energy of such a molecular complex is given by the sum of the electrostatic energy (which also contains the contribution from electrostatic repulsion), and the charge-transfer resonance energy. As mentioned above the lifetime of the positronium atoms will be determined by the time it spends on the average in a location of increased electron density, e.g., in a Ps complex, and will thus be directly related to the stability of such a Ps complex.

If we consider first the neutral (diamagnetic) molecules listed in Table I, it can be seen that the group of compounds which show only weak interactions with Ps are also those known as weak acceptor molecules.[23]

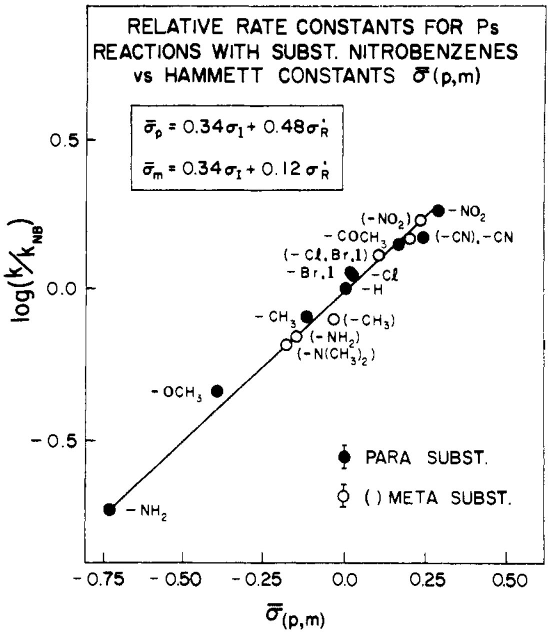

Figure 3. Relative rate constants log (K_{obsd}/K_{NBobsd}) plotted as a function of Hammett's constants σ_I and σ_R^+. Temperature, 20°; reactions were carried out in dilute benzene solutions. The substrate concentration ranged usually from 0 to 50 mmol.

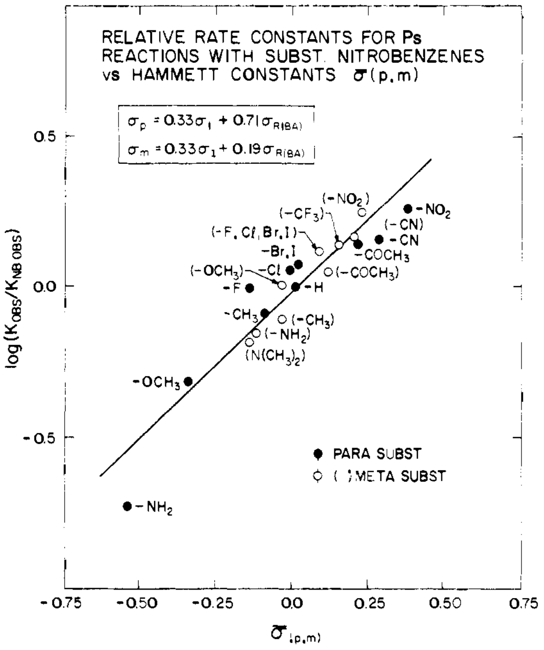

Figure 4. Relative rate constants log (K_{obsd}/K_{NBobsd}) plotted as a function of Hammett's constant $\sigma_{R(AB)}$ and σ_I. Experimental conditions same as in Figure 3.

In the case of the simple aliphatic hydrocarbons which have no dipole moments one would expect that mainly London dispersion forces are operative in holding the Ps-substrate complex together and the stability of these complexes should therefore be very small and mainly related to the electronic polarizability of the substrate molecule (if differences in the collision frequencies are neglected). Such a correlation has indeed been found between the rate constants K_{obsd} for Ps reaction and the electronic polarizibilities of these molecules.[3,4,27,28] Since parachor and surface tension are also closely related to the polarizability, it is not surprising that other investigators found similar correlations between these parameters and the Ps reactivities toward these molecules.[13,27-30]

On the other hand the highly reactive (diamagnetic) neutral organic substances listed in Table I are uncharged π electron compounds and contain highly electronegative elements such as oxygen and nitrogen. All of them have been shown to be strong electron acceptors and form stable molecular complexes.

The effect of the nature of the acceptor species on the reactivity toward Ps follows broadly the order as expected from the stability of these molecular complexes with conventional donors.[23] In the case of substituted nitrobenzenes the rate constants of their reactions with Ps reflect the electron-withdrawing power of the substituent group in the acceptor molecules. This is shown in Figures 3 and 4 where an attempt has been made to fit the observed rate constants (K_{obsd}) for the para- and meta-substituted nitrobenzenes to the linear free energy function varying the nature of the parameter σ_R (resonance contribution) as defined by Ehrenson et al.[31]

$$\bar{\sigma} = \rho_I\sigma_I + \rho_R\sigma_R$$

The quality of different fits was tested and the bilinear equation

$$\log K_{obsd}/K_{NBobsd} = \rho_I\sigma_I + \rho_R\sigma_R$$

solved to obtain ρ_I and ρ_R, where K_{obsd} is the rate constant for a particular nitrobenzene derivative and K_{NBobsd} is the rate constant for nitrobenzene. The ρ_I for the meta derivatives should equal the ρ_I for the para derivatives because any differences are only due to resonance effects (ρ_R). The best fits were obtained using σ_R^+ values (electrophilic attack), Figure 3, and $\sigma_{R(BA)}$ values for σ_R (Figure 4). For σ_R^+

$$\sigma_p = 0.34\sigma_I + 0.40\sigma_R^+,\ SD = 0.053,\ f = 0.20$$

$$\sigma_m = 0.34\sigma_I + 0.11\sigma_R^+,\ SD = 0.029,\ f = 0.21$$

The para derivatives give a large resonance effect as expected, the ratio ρ_R/ρ_I for para derivatives being 1.18 in comparison to a value of only 0.33 for meta derivatives. For $\sigma_{R(BA)}$

$$\bar{\sigma}_p = 0.33\sigma_I + 0.71\sigma_{R(BA)},\ SD = 0.089,\ f = 0.34$$

$$\bar{\sigma}_m = 0.33\sigma_I + 0.19\sigma_{R(BA)},\ SD = 0.037,\ f = 0.28$$

giving a ratio, ρ_R/ρ_I, for para derivatives of 2.15 compared with 0.58 for meta derivatives.

This is consistent with the expected trend that resonance effects are of less importance in meta-substituted compounds. (SD is the standard deviation and f is defined as the standard deviation divided by the root mean square of the data points.)

Further evidence for the contention that the Ps reactions obey normal chemical reactivity scales has been obtained from the stereospecificity of the Ps reactions.

As shown in Table II where the observed rate constants K_{obsd} are listed for a series of nitrobenzene derivatives, substitution on a carbon adjacent to a nitro group causes in several cases a significant lowering of the reaction rate that can be attributed to steric effects. This effect is most pronounced, as expected, when there is a bulky substituent ortho to the nitro group. For example, K_{obsd} for *o*-nitrotoluene is definitely smaller than that for *m*- or *p*-nitrotoluene. Similar steric effects are observed for the ortho isomers of dinitrobenzene, nitrobenzoic acid, nitroanisole, iodo-, bromo-, chloro-, and fluoronitrobenzenes, and nitro-α,α,α-trifluorotoluene, nitrobenzyl alcohol, and nitroaniline. (The latter is compared with its meta isomer.)

The ortho effect and steric inhibition of the positronium reaction can be associated with the degree of coplanarity of

Table II. Rate Constants K_{obsd} for the Reaction of Thermal *o*-Ps Atom with Nitrobenzene Derivatives in Dilute Benzene Solutions (at 20°)[a]

Compd	Rate constant $K \times 10^{-10}$, M^{-1} sec^{-1} (±0.2)	Compd	Rate constant $K \times 10^{-10}$, M^{-1} sec^{-1} (±0.2)	Compd	Rate constant $K \times 10^{-10}$, M^{-1} sec^{-1} (±0.2)
Nitrobenzene	2.7	1-Fluoro-2-nitrobenzene	2.9	2-Nitrophenyl acetate	2.3 (±0.1)
		1-Fluoro-3-nitrobenzene	3.5	4-Nitrophenyl acetate	2.6 (±0.1)
2-Nitroaniline	1.0	1-Fluoro-4-nitrobenzene	2.7		
3-Nitroaniline	1.9			2-Nitrobenzoic acid	2.0
4-Nitroaniline	0.51 (±0.06)	1-Chloro-2-nitrobenzene	2.5	3-Nitrobenzoic acid	2.8
		1-Chloro-3-nitrobenzene	3.5	4-Nitrobenzoic acid	2.9 (±0.5)
3-Nitro-*N,N*-dimethylaniline	1.8	1-Chloro-4-nitrobenzene	3.1	2-Nitroacetophenone	3.0
2-Nitrophenol	3.3	1-Bromo-2-nitrobenzene	2.2	3-Nitroacetophenone	3.0
3-Nitrophenol	2.6	1-Bromo-3-nitrobenzene	3.6	4-Nitroacetophenone	3.8
4-Nitrophenol	1.3	1-Bromo-4-nitrobenzene	3.2		
				2-Nitrobenzaldehyde	3.2
2-Nitroanisole	0.49 (±0.08)	1-Iodo-2-nitrobenzene	2.3	3-Nitrobenzaldehyde	3.5 (±0.1)
3-Nitroanisole	2.7	1-Iodo-3-nitrobenzene	3.5	4-Nitrobenzaldehyde	4.0
4-Nitroanisole	1.3	1-Iodo-4-nitrobenzene	3.2		
				2-Nitro-α,α,α-trifluorotoluene	2.5 (±0.1)
				3-Nitro-α,α,α-trifluorotoluene	3.8 (±0.1)
2-Nitrotoluene	0.85 (±0.20)	2-Nitrobenzyl alcohol	2.0		
3-Nitrotoluene	2.1	3-Nitrobenzyl alcohol	2.4		
4-Nitrotoluene	2.2	4-Nitrobenzyl alcohol	2.5 (±0.1)	Nitromethane	3.5
				Nitroethane	5.0
2-Nitrobenzonitrile	3.9	1,2-Dimethyl-3-nitrobenzene	0.34 (±0.06)		
				1-Nitropropane	5.2
3-Nitrobenzonitrile	3.9	1,2-Dimethyl-4-nitrobenzene	1.8		
				2-Nitropropane	4.9
4-Nitrobenzonitrile	3.9 (±0.1)	1,3-Dimethyl-2-nitrobenzene	0.039 (±0.003)		
				Anisole	4.4
		1,3-Dimethyl-5-nitrobenzene	2.2		
				Benzaldehyde	5.1
1,3-Dinitrobenzene	4.7	2,4-Dinitrophenylhydrazine	3.1 (±0.5)	Acetophenone	6.1
1,4-Dinitrobenzene	5.0	2,2-Diphenyl-1-picrylhydrazyl (DPPH)	3.8 (±0.1)		
		1,3,5-Trinitrobenzene	5.5		
		1-Nitronaphthalene	2.65		
		Nitrosobenzene	3.5		
		Benzil	0.138 (±0.020)		
		α-Nitrotoluene	0.015 (±0.002)		

[a] Measurements were carried out over a wide concentration range depending on the reactivity of the compound usually from 0 to 50 mM, except in the case of very unreactive solutes where higher concentrations were used. Rate constants quoted are the average of at least eight measurements (made with different solute concentrations). The intensity of the long lived component, I_2, varied only slightly under these conditions. Its value usually decreased by no more than 10% of the initial value observed in the pure solvent, which was 38% in benzene (at 25°).

the nitro group and the aromatic ring. Rotation of the nitro group out of the plane of the benzene caused by the presence of a bulky substituent ortho to the nitro group lowers the amount of π-electron overlap between the nitro group and the ring, and thus reduces the reactivity.

The halonitrobenzenes clearly illustrate the ortho effect of such bulky substituents toward positronium annihilation. In the case of the fluoronitrobenzene, the small size and smaller steric effect of the fluorine atom causes a weaker ortho effect of the fluoro derivative in comparison with the ortho halogens.

A similar explanation can be invoked for the nitrobenzonitriles where the size of the linear cyanide group is relatively small and no steric effect occurs. This importance of delocalization between the nitro group and the ring is further supported by the rate constant data for the nitrophenol derivatives. The rate constant data are the reverse of the usual ordering and have $k_p < k_m < k_o$. This can be attributed to hydrogen bonding between the hydroxyl group and the electronegative nitro group in the ortho derivative. Thus the nitro group is rigidly held in the plane of the benzene ring by this bond; hence no ortho effect is observed.

An even more dramatic demonstration of the effect of the various degrees of steric interaction can be found in the case of the isomers of the dimethylnitrobenzene. The small changes in the rate constants of 1,3-dimethyl-5-nitrobenzene and 1,2-dimethyl-4-nitrobenzene can be attributed to the inductive effects of the methyl groups, since no steric interaction is expected. However, as the nitro group is gradually surrounded by methyl groups going from 1,2-dimethyl-3-nitrobenzene to 1,3-dimethyl-2-nitrobenzene the steric effect lowers the rate constants tenfold and a hundredfold, respectively (Figure 5).

In this conjunction it seems interesting to note that when the nitro group is separated from the aromatic ring by a CH_2 group or attached to an aliphatic group (Figure 6) the reactivity toward Ps is greatly diminished. This again emphasizes that the combination of nitro group and conjugated system is responsible for the enhanced reactivity toward Ps.

The importance of the degree of conjugation available in the acceptor for Ps reactivity or Ps complex formation becomes also clearly visible by comparing the rate constants for the fully conjugated *p*-benzoquinone, maleic anhydride,

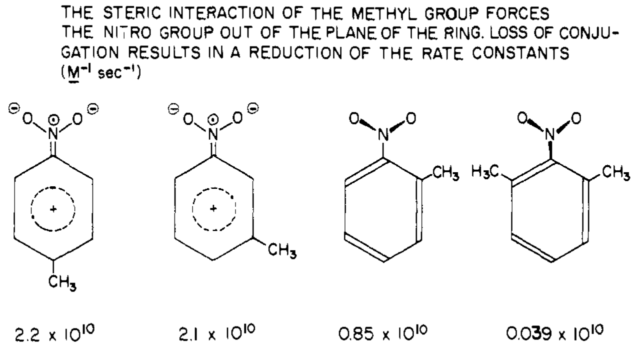

Figure 5. Demonstration of the steric effect on the Ps rate constants (K_{obsd}) by introducing methyl groups in ortho position in the nitro group. (K_{obsd} measured in dilute benzene solutions at 20°.)

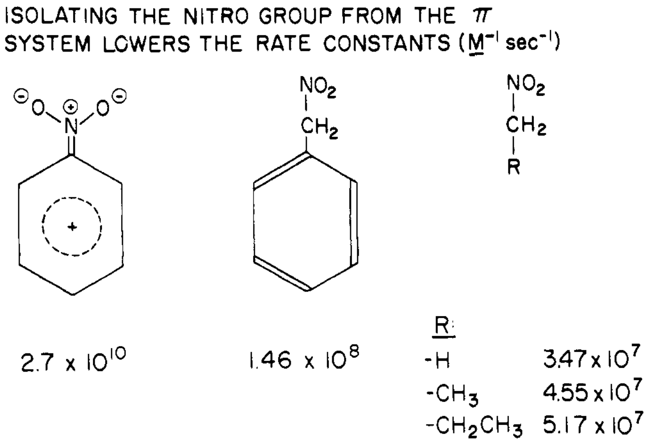

Figure 6. Demonstration of the effect of conjugation on Ps rate constants (K_{obsd}) in various nitro compounds. (K_{obsd} measured in dilute benzene solutions at 20°.)

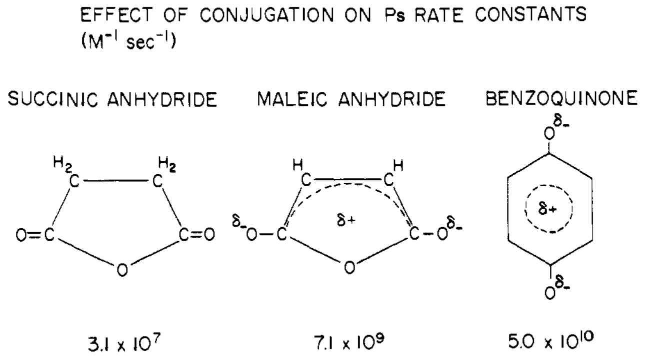

Figure 7. Demonstration of the effect of conjugation on the Ps rate constants K_{obsd} in cyclic anhydrides. (K_{obsd} measured in dilute benzene solutions at 20°.)

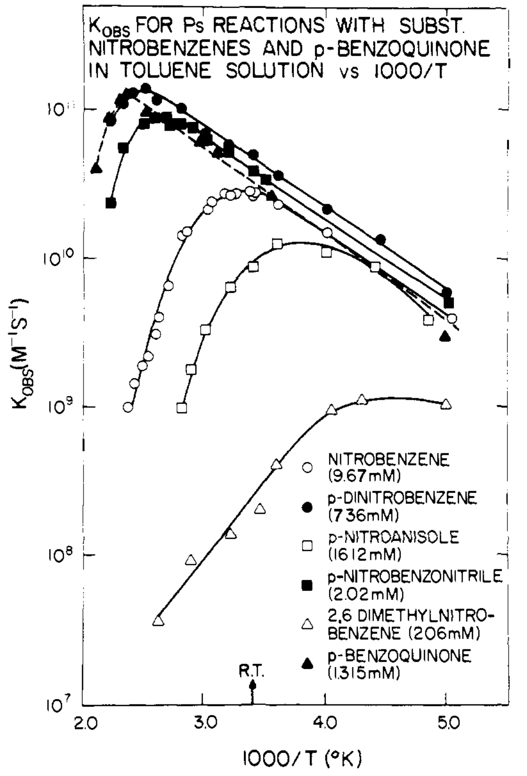

Figure 8. Observed rate constants (K_{obsd}) for thermal o-Ps reaction with various substrates in dilute toluene solutions as a function of the reciprocal temperature (in °K).

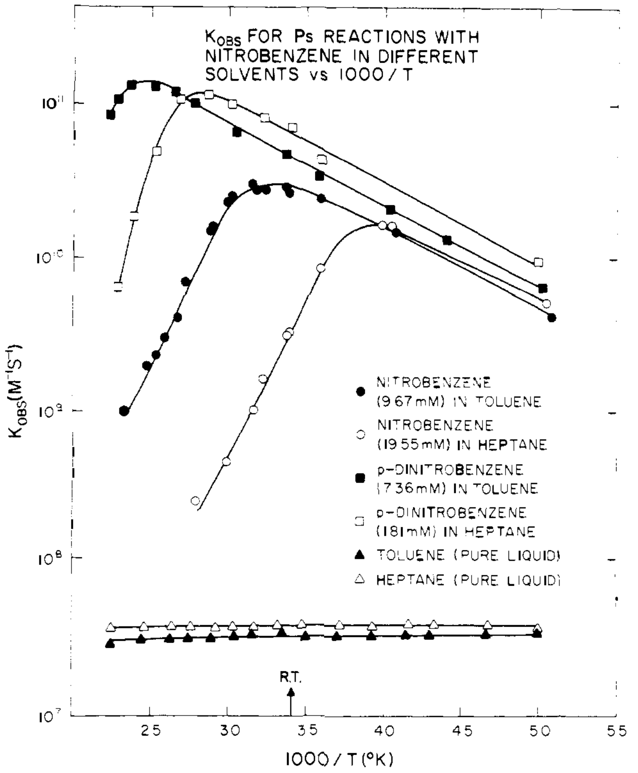

Figure 9. Observed rate constants (K_{obsd}) for thermal o-Ps reaction with nitrobenzene or p-dinitrobenzene in dilute toluene and heptane solutions as a function of the reciprocal temperature (in °K).

and benzil molecules with those of succinic anhydride and acetophenone, where no conjugation exists (Figure 7).

All these results closely parallel those which have generally been observed for conventional chemical donors with the same acceptor molecules. They, by analogy, suggest that the interaction between Ps and these molecules proceeds via a complex similar to those postulated for typical molecular complexes.

(c) **Temperature Studies.** To further characterize and to provide simultaneously additional supporting evidence for the Ps complex model a series of temperature studies was carried out with a selected number of these molecules. From Figure 8 or 9 where K_{obsd} is plotted vs. the reciprocal of the temperature (in °K) it can be seen that at low temperatures K_{obsd} increases with increasing temperatures in accordance with the Arrhenius equation. At higher temperatures K_{obsd} shows a maximum and declines with a further increase of temperature.[32] This type of deviation process involves an equilibrium as indicated in eq 1 and thus can be

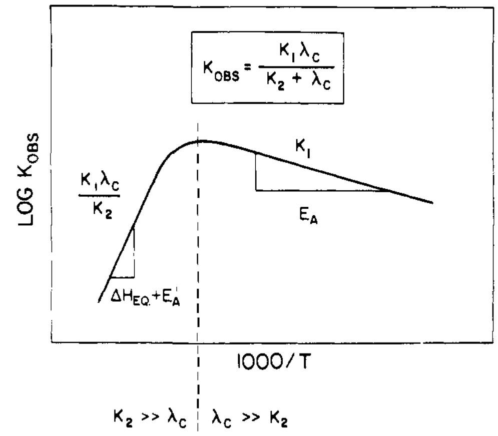

Figure 10. Plot of log K_{obsd} vs. 1000/T (schematic representation).

taken as supporting evidence for the postulated Ps complex formation-decomposition model.[35,36]

At low temperature, one can postulate that λ_c, the annihilation constant for positron bound in the complex, is considerably larger than K_2, the rate constant for decomposition of the Ps complex, and K_{obsd} will therefore be equal to K_1 (Figure 10). Thus from this part of the plot the Arrhenius activation energy, E_A, for the process

$$\mathrm{Ps} + \mathrm{M} \xrightarrow{K_1} \mathrm{PsM}$$

and since E_A is related to the enthalpy change $\Delta H^\ddagger$ for the activated complex by the equation $E_A = \Delta H^\ddagger - RT$, $\Delta H^\ddagger$ can be assessed (Figure 11).

As can be seen from Table III the activation energies are very small, ~1 kcal/mol, and constant (within the experimental error) for the series of nitrobenzene derivatives studied and for p-benzoquinone. K_1, however, and thus $\Delta G^\ddagger$, the free energy of activation, shows again a distinct dependence on the chemical nature of the compound. It follows roughly the same pattern as previously discussed (vide supra) for K_{obsd}, the reactivity showing the following trend, p-dinitrobenzene > nitrobenzonitrile > nitrobenzene > p-nitroaniline.

The particularities of the experimental method employed, in which λ_2 is first measured in the pure solvent ($\lambda_2 = \lambda_p$, see above) under the same conditions, temperature, etc., and subsequently with the substrate present, assure that the observed rate constant is not affected by viscosity changes or changes in the diffusion rate of the Ps atom.

Therefore the activation energies which are fairly constant for all systems studied cannot represent the activation energy of viscosity and one would have to argue that the changes in the forward rate constant K_1 are caused to a substantial degree by changes in the preexponential factor, A, of the Arrhenius equation or by differences in $\Delta S^\ddagger$, the entropy of activation.

From Figure 8 it can be seen that the high-temperature part of the plot log K_{obsd} vs. $1/T$ results again in a series of straight lines. Since the lifetime of the positron in the Ps complex is solely controlled by the electron density at the location of the positron and not by normal thermodynamic factors, one can make the reasonable assumption that the energy of activation for positron annihilation (E_A') is zero. Then according to the proposed Ps complex formation-decomposition model from the slope of these lines ΔH_{EQ}, i.e., the enthalpy associated with the equilibrium process

$$\mathrm{Ps} + \mathrm{M} \rightleftharpoons \mathrm{PsM}$$

can be evaluated (Figures 10 and 11).[38]

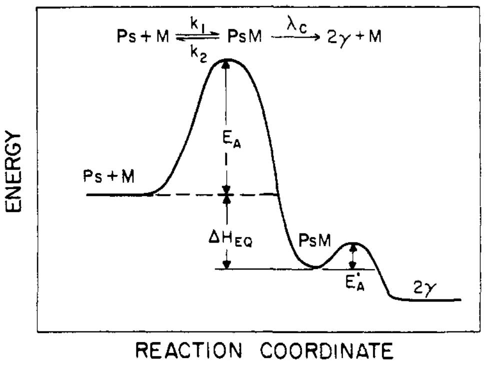

Figure 11. Energy diagram for the process (schematic) Ps + M $\rightleftharpoons$ PsM $\rightarrow 2\gamma$.

Table III. Thermodynamic and Kinetic Data Obtained for the Reactions of Thermal o-Ps Atoms with Various Substrates in Dilute Toluene or Heptane Solutions[a]

	E_A, kcal/mol	ΔH_{EQ}, kcal/mol	$K_1 \times 10^{-10}$ M^{-1} sec^{-1} (at −23°)
Nitrobenzene derivative (in toluene)			
p-NO$_2$	1.1 ± 0.2	n.d.	2.2 ± 0.2
p-CN	1.0 ± 0.1	−6.0 ± 0.5	2.0 ± 0.2
H	0.8 ± 0.1	−4.5 ± 0.3	1.6 ± 0.2
p-CH$_3$O	0.9 ± 0.1	−3.6 ± 0.3	1.1 ± 0.2
2,6-Dimethyl		−2.7 ± 0.3	
p-NH$_2$		−1.1 ± 0.1	
(In heptane)			
H	1.3 ± 0.2	−4.4 ± 0.4	1.6 ± 0.2
p-CH$_3$O	1.2 ± 0.4	−2.9 ± 0.4	
p·NO$_2$	1.0 ± 0.2	−8.0 ± 0.6	3.0 ± 0.2
p-Benzoquinone (in toluene)	1.0 ± 0.3	−7.5 ± 0.5	1.8 ± 0.2
Toluene (pure)		~0.0	
Heptane (pure)		~0.0	

[a] K_1 values at −23° obtained from graph K_{obsd} vs. $1/T$. E_A = energy of activation for process Ps + M → PsM. ΔH_{EQ} = enthalpy change associated with the equilibrium Ps + M $\rightleftharpoons$ PsM. E_A' = energy of activation for positron annihilation of positron in complex assumed to be zero.

These enthalpies, ΔH_{EQ}, are listed in Table III. They confirm the order of complex stability that one would expect from the electron withdrawing or donating properties of the substituents in the nitrobenzene derivatives.

This also is consistent with the proposed model that in the case of toluene, heptane, or other unreactive substances ΔH_{EQ} approaches 0; i.e., these compounds show very little tendency to act as acceptor molecules in molecular complexes.

(c) **The Role of Solvent Effects in Ps Complex Formation.** So far solvent effects have been provisionally neglected. However, it is quite clear that solvating effects should play an important role in the case where the formation of the Ps molecular complex may result in a partial electron transfer and build-up of positive or negative charges on the two components. The presence of a solvent may thus stabilize the complex to a different degree depending on the nature of the solvent.

Figure 9 shows a plot of K_{obsd} vs. $1/T$ for nitrobenzene and p-dinitrobenzene in toluene and heptane. An evaluation of E_A and ΔH_{EQ} (Table III) shows no significant changes in these two parameters; however, Figure 9 reveals definitely a drastic change in $K_{obsd} = K_1\lambda_c/(K_2 + \lambda_c)$. If one assumes that λ_c is not affected by the solvent change and K_1 only slightly so (see Figure 9), then changes in K_2 and thus in $\Delta G^\ddagger$ for complex formation must be mainly responsible for the observed differences in the two solvents. Since ΔH_{EQ} was found to be rather solvent independent for a given substrate molecule (see Table III), this would indicate that entropy effects determine to a major extent the variation of the stability of these complexes in different solvents.

Conclusion

Positronium atoms behave in much the same way as normal chemical compounds. They undergo chemical reactions (equilibria and competition reactions) in reactive media, where Ps molecular complex formation is strongly favored by the presence of an appreciable amount of intermolecular interaction energy. They are fairly unreactive in an environment where such forces are relatively small.

The activation energies for the process

$$\mathrm{Ps} + \mathrm{M} \xrightarrow{K_1} \mathrm{PsM}$$

are very small (~1 kcal/mol). Differences in the observed rate constants have to be attributed to the preexponential Arrhenius factor.

The enthalpy associated with the equilibrium involved in the formation of the Ps complexes studied in this investigation ranges from 0 for toluene or heptane to 8 kcal for the most reactive species *p*-dinitrobenzene or *p*-benzoquinone.

Solvent effects seem to be responsible for a variation of the stability of these complexes in different media. They have been tentatively attributed to changes in the entropies involved in the Ps complex formation.

In conclusion it could be stated that with our enhanced understanding of the Ps reactions new methods have been opened up by which the electron acceptor properties and related parameter such as the electron affinities, electron acceptor abilities, etc., of a large number of molecules can be conveniently studied in solution or in the gas phase. Furthermore, positronium reactions provide a rather simple technique to investigate the stabilizing effect of the solvent on the molecular complex and should allow a scale to be set up for the effective solvating power of solvents.

Last but not least it should be pointed out that positronium chemistry might well provide the extra impetus to observe tunneling since the tunneling ability of Ps is very high because of its low reduced mass. While low temperatures are required for a proton to tunnel significantly, the Ps atom tunnels at high temperatures, well above room temperature. Experiments to study this phenomenon by Ps reactions are presently being carried out.

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(1) Work supported by the U.S. Atomic Energy Commission.

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(25) A more complete mechanism would include the solvent as an active species.

$$2\gamma \longleftarrow \mathrm{PsS} \overset{\mathrm{S}}{\rightleftharpoons} \mathrm{Ps} \overset{\mathrm{M}}{\rightleftharpoons} \mathrm{PsM} \longrightarrow 2\gamma \qquad (2a)$$

The solvent (S) and reactant (M) compete for the positronium atoms and two separate equilibria are set up. However, a rigorous mathematical treatment of this mechanism shows that it would be very difficult to interpret the experimentally accessible data in terms of this expanded mechanism (eq 2a). Therefore, throughout this investigation the simplified scheme (eq 2) was applied (λ_p = const).

(26) It should be pointed out that eq 6 is strictly valid only when $(\lambda_c + \lambda_p + K_1[\mathrm{M}] + K_2)^2 \gg 4(K_1[\mathrm{M}]\lambda_c + \lambda_p(\lambda_c + K_2))$. In the present experiments this condition is usually satisfactorily fulfilled, typically: 10^{19} sec^{-1} $\gg$ 10^{18} sec^{-1}.

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(32) The changing, nonparallel slopes of some of the Arrhenius plots at room temperature are rather disturbing. They make the Hammett parameter comparison with the relative rate constants somewhat questionable, and it would be difficult in view of the observed temperature dependence of K_{obsd} to draw any conclusions as to the type of reaction, electrophilic, nucleophilic, etc. Despite the rate constants of these compounds being incompatible (nonparallel) with other nitrobenzene derivatives at room temperature the Hammett parameters data give a good correlation (Figures 3 and 4). This suggests that these specific Hammett parameters determined by comparing classical organic reactions inherently include this same room temperature incompatability. There is very little published evidence of Hammett parameter studies along classical lines,[33,34] in which the temperature of the reaction medium is varied over a wider range.

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(35) However, other mechanisms can be postulated to explain the temperature data. Two coexistence species of the quenching molecule with a temperature dependent equilibrium could exist. One species (M_1) reacts rapidly with positronium, but the other species (M_2) is inert.

$$\begin{tikzcd}
\mathrm{Ps} + \mathrm{M_1} \arrow[r, "K_1"] \arrow[d, shift left, "K_{eq}"] & \mathrm{PsM_1} \arrow[r, "K_2"] & 2\gamma \\
\mathrm{M_2} \arrow[u, shift left]
\end{tikzcd}$$

This mechanism contains an inhibition equilibrium, and PsM_1 immediately annihilates when it is formed. The resultant expression for the observed rate is $K_{obsd} = K_1/(1 \% K_{eq})$. Assume that the inert species M_2 is preferentially formed at high temperatures. At low temperatures K_{eq} is small and $K_{obsd} \cong K_1$; at high temperatures K_{eq} is large and $K_{obsd} \cong K_1/K_{eq}$, and as the temperature increases K_{obsd} decreases in magnitude. The ortho effect and rotation of the nitro group out of the plane of the aromatic ring can be introduced into this mechanism for nitrobenzene derivatives. M_2, the unreactive species, has the nitro group out of the plane of the aromatic ring; M_1 has the nitro group planar and conjugated to the ring. As the temperature is raised vibrational and rotational effects force the nitro group out of the plane of the ring, resulting in the formation of larger concentrations of the unreactive species M_2. Benzoquinone should have no similar rotational effect, hence Arrhenius behavior would be expected if the rotational postulate were correct. A temperature study of benzoquinone has shown non-Arrhenius behavior and certainly does not support a nitro group rotation mechanism. On the other hand, M_1 may be another type of structure (e.g., charge transfer complex) and this coexistent species mechanism cannot be ruled out by the benzoquinone result. However, the fact that the *same* behavior is observed not only in toluene but also in heptane solution, where EDA complex between nitroaromatics and heptane has not been observed, would make this alternative very unlikely.

(36) A slightly different explanation of the temperature dependence of the

rates of positronium reactions with diamagnetic organic molecules in liquids was offered by Goldanskii et al.[22] on the basis of the "bubble" model. Tao et al.[37] suggest that Ps may not be fully thermalized when it reacts and thus causes the deviations from the $K \propto 1/T$ correlation.

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(38) It should be noted that if the positron annihilation includes another step, e.g., the complete electron transfer in the Ps complex leading to $e^+ + M^-$, then E_A' would represent the energy of activation for this process and thus $\neq 0$.

Relative Rate Constants for the Reaction of O(^{3}P) Atoms with Selected Olefins, Monoterpenes, and Unsaturated Aldehydes

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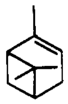
Abstract: Using a competitive technique, rate constants for the gas phase reaction of O(^{3}P) atoms with selected monoterpenes, unsaturated aldehydes, and olefins have been determined relative to that for the reaction of O(^{3}P) atoms with cyclopentene at 296 ± 2 K. The rate constants obtained, relative to cyclopentene as unity, were: propylene (0.181 ± 0.010), α-pinene (1.38 ± 0.05), β-pinene (1.30 ± 0.05), *d*-limonene (5.61 ± 0.45), 1-methylcyclohexene (4.21 ± 0.17), 1,3-cyclohexadiene (4.33 ± 0.20), ketene (0.024 ± 0.003), acrolein (0.020 ± 0.002), and crotonaldehyde (0.044 ± 0.005). These relative rate constants have been placed on an absolute basis using the recent literature room temperature rate constant for the reaction of O(^{3}P) atoms with propylene, $k(\text{propylene}) = 2.10 \times 10^9$ l. mol^{-1} sec^{-1}, and those for ketene, acrolein, and crotonaldehyde are compared and discussed with existing literature values.

The reactions of ground state oxygen atoms with simple olefins, alkenes, and, to a lesser extent, aromatic hydrocarbons have been extensively investigated.[1-3] However, little work has been reported on the products and rate constants for the reaction of O(^{3}P) atoms with unsaturated aldehydes and the naturally occurring monoterpene (C_{10}) hydrocarbons.[1,2]

Recently there has been considerable interest in these systems, not only from the fundamental grounds of structure and reactivity but also because of their possible significance in the chemistry of polluted atmospheres. Thus for example, the monoterpene hydrocarbons such as α-pinene (I), β-pinene (II), and *d*-limonene (III) have been shown to be emitted into the atmosphere by plant life,[4] and on a global basis have been proposed to be the major source of atmospheric hydrocarbon.[4] Accordingly, the role that these terpenes may play in air pollution chemistry has been studied by a number of investigators.[4-10] Terpenes have been shown to form large amounts of aerosol when photooxidized[5] or allowed to react with ozone in air,[6] and the aerosol from their reaction with ozone is thought to be the source of the blue haze phenomenon observed in forested areas.[7] Furthermore, peroxyacetyl nitrate and aldehydes have been found as products in the photooxidation of pinene.[8] Recently NO_x photooxidation[9] and ozonolysis rate studies[9,10] for a number of monoterpene reactions have been reported which show these compounds to be highly reactive.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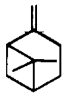
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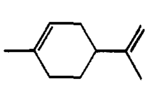
III

The oxidation of unsaturated aldehydes and ketene are also of particular interest both fundamentally and because of their role in photochemical smog. Thus ketene, acrolein, and crotonaldehyde are toxic and are powerful lachrymators. Indeed, acrolein has been detected in ambient air[11] and is considered to be one of the contributors to intense eye irritation accompanying photochemical smog because of its stability to photochemical oxidation and direct photolysis.[12] The possible presence of ketene in polluted urban atmospheres has been previously postulated,[13] and ketene has been shown to be produced from gas phase ozone-olefin reactions under a variety of conditions.[14-17]

Because of the considerations cited above, as part of a broader investigation into the rates and products of the reactions of O(^{3}P) atoms with unsaturated organic compounds involved in the formation of photochemical air pollution, we have determined room temperature rate constants for the reactions of O(^{3}P) atoms with ketene, acrolein, crotonaldehyde, α-pinene, β-pinene, *d*-limonene, 1-methylcyclohexene, and 1,3-cyclohexadiene relative to that for the reaction of O(^{3}P) atoms with cyclopentene. The reaction of O(^{3}P) atoms with cyclopentene has been thoroughly investigated[18] and has been extensively used to determine relative O(^{3}P) atom reaction rate constants by Cvetanovic and coworkers.[1,19]

In order to test the experimental system and to place the relative rate constants on an absolute basis, propylene was included in the compounds studied, as its absolute room temperature rate constant is known to a high degree of accuracy.[3,20-23]

Experimental Section

Ground state O(^{3}P) oxygen atoms were generated by the mercury photosensitization of nitrous oxide at 2537 Å:

$$\text{Hg}(6^1S_0) + h\nu \rightarrow \text{Hg}(6^3P_1) \qquad \text{(Ia)}$$

$$\text{Hg}(6^3P_1) + N_2O \rightarrow \text{Hg}(6^1S_0) + N_2 + O(^3P) \qquad (1)$$

In order to minimize short wavelength photolysis of the reactants and products, the 2537 Å resonance radiation from a low pressure mercury arc was passed through a Corning 7-54 filter to remove