energies for the title reactions increase with increasing chlorine substitution of the radicals and the unsaturated C_2 species, and β sites are the preferred addition sites. In addition, barrier heights for the addition C_2 radicals were lower than those for C_1 additions, a result that is consistent with the more abundant production of C_4 and C_6 species, as opposed to C_3 and C_5, in the pyrolysis of C_1 and C_2 chlorohydrocarbons. It should be recognized, however, that although the individual activation energies calculated may not be absolutely accurate the trends presented here should be of considerable utility in predicting the relative magnitudes of activation energies of these related reactions. Once more accurate reaction rate data on specific reactions become available, the results presented here can be calibrated to better predict activation energies of the remaining reactions with greater accuracy.

Acknowledgment. This research was supported by funds from the U.S. Environmental Protection Agency, Grant R815136-01-0. We also thank M. Kassem for his useful discussions.

Multiphoton Ionization of Phenol in Nonaqueous Solutions: Characterization of the Cation and Ion–Molecule Chemistry

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The phenoxy cation has been generated in polar and nonpolar solutions by two-photon ionization of phenol by using 2.5-ns pulses of 266-nm light. The ions have been characterized by pulsed conductivity (ion mobility) measurements and transient absorption spectroscopy with λ_{max} = 290–300 nm and an estimated extinction coefficient of 1300 M^{-1} cm^{-1}. The involvement of the phenoxy ion in ion–molecule chemistry with either neutral solute or sovlent molecules has also been observed. The kinetics of these processes as well as a proposed reaction mechanism are presented.

Introduction

Considerable research effort has been concentrated on determining the effects of ionizing radiation on organic solutions.[1] The goal of this type of research is to characterize the entire reaction mechanism, i.e. the conversion of particle or photon energy into internal energy of solute or solvent, but the experimental studies tend to be most concerned with the transient species created by the initial interaction of ionizing radiation and particle. The transient species in the case of energetic particle excitation may be either ionic or radical in nature and electron beam impact (pulse radiolysis) is typically the energy source for liquid-phase experiments.

Multiphoton production of energy-selected ions has been shown to be an effective technique for production of ions in the gas phase. Furthermore, it has been shown that these ions may be used in unimolecular reaction studies or as reactants in ion–molecule chemistry.[2] Although the gas-phase studies suggest that these same techniques would be useful in liquid-phase ion–molecule chemistry, the use of multiphoton techniques for such experiments has not been widely reported. However, multiphoton techniques have been employed in other types of studies involving liquids. Among these are the use of visible wavelength photons to probe UV–visible electronic transitions[3a,b] and two-photon production of geminate pairs for the observation of recombination kinetics.[3c] We recently reported two multiphoton-induced chemistry (MPIC) studies of aromatic molecules in polar and nonpolar solvents,[4,5] and two other brief communications involving this technique have appeared.[6] In these MPIC experiments, the nonlinear technique was used to created reactant ions that were then observed to react with both neutral solute and solvent molecules. The experiments from our laboratory were long-term photo-pumping and pulsed conductivity measurements. Therefore, the exact nature of the reaction mechanism, and even the active species, had to be inferred from the nature of the products formed in the process. In this report, we present further evidence of the ion–molecule nature of the reaction initiated by MPI by reporting additional photopumping and pulsed conductivity data but also real-time observations of the cation involved in the reaction.

The target molecule, in this instance, is phenol. The neutral UV-induced photochemistry of phenol has been well-studied.[7] Phenol has been observed to undergo fragmentation from the $\pi\pi^*$ state to form the phenoxy radical. This process has been observed in water, alcohols, and hexane. Identical chemistry was observed in the photolysis of anisole and the phenoxy anion. The final product in the reported photochemistry has been shown to be isomeric biphenyldiols. Our previous results have shown that the ion–molecule product for phenol chemistry is phenoxyphenol (in hexane). Similarly, analogous photoproducts consistent with ion–molecule mechanisms have been observed for nitrobenzene and anisole. It is obvious that a new reaction channel is available, and the current results serve to identify this pathway. Subsequent subsections describe photochemical, pulsed conductivity, and transient absorption measurements. These data sets are then utilized to identify the reaction channel and characterize the reactants in the ion–molecule chemistry.

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Experimental Section

Experiments involving long-term photo-pumping and pulsed conductivity measurements and transient absorption spectroscopy were conducted. In all cases, the light source was a Quanta Ray DCR11 Nd:YAG laser with appropriate harmonic crystals and an harmonic separator accessory.

Photo-pumping studies utilized a specially constructed 5-cm stainless steel cube cell. Full details of the operation of this device have been previously reported,[5] and are only briefly described here. Two of the six available ports are fitted with S1-UV quartz windows for coupling to the light source via a 15-cm focal length lens. All seals were made with Teflon o-rings. The sample volume in this configuration was 2 cm^3. Irradiation time and laser intensity were wavelength dependent and selected so as to produce a total reactant consumption of approximately 10% or less. For 355-nm (τ = 6 ns, 0.5 mJ/pulse $\leq E \leq$ 15 mJ/pulse) radiation, 1-h exposure, at 10 Hz, resulted in a total irradiation time of 216 μs. At 266 nm (τ = 2.5 ns, 0.01 mJ/pulse $\leq E \leq$ 1.0 mJ/pulse), both 1-h and 20-min exposures were employed, resulting in total irradiation periods of either 90 or 30 μs. The solutions of phenol were 0.001 M for 266-nm photolysis, but increased to 0.12 M for 355-nm radiation due to the decreased absorption cross sections. Samples were filtered through micropore syringe filters and purged, with N_2, Ar, O_2, or SF_6, as required. Photoproducts were identified and analyzed by quantitative GC/MS on a Finnegan 4000 spectrometer. In these studies, products were identified by comparison of GC retention times and mass spectra. Reactant consumption and product formation were determined by reference to a standard curve by using known samples and dodecane as an internal standard. Dodecane was shown, in separate experiments, not to undergo any photochemistry at the wavelength used in this study. Typically the dodecane concentration was 8.8 $\times$ 10^{-3} M for the photo-pumping studies reported here.

The pulsed conductivity measurements utilized the same stainless steel cell described above, but reconfigured into a more appropriate form. The two ports located perpendicular to the quartz windows were fitted with stainless steel electrodes inserted through Teflon or Macor insulators. Two different electrode configuration were possible: an opposing pair of 6-mm-diameter cylindrical electrodes and a pair of 5 cm × 0.6 cm rectangular electrodes. The results reported here were obtained with the second configuration, since the length of the electrodes permitted conductivity measurements with relatively concentrated solutions of target molecules. Routine measurements involved solutions of 10^{-5} M phenol in solvent. The electrode spacing was varied between 1 mm and 5 mm and a voltage of 1–6 kV was typically applied, so that fields of the order of 2–10 kV/cm were possible. The cell was kinematically mounted on a translation stage so that positioning was reproducible and readily controlled. The laser beam was focused into approximately the center of the cell by lenses of various focal lengths, but primarily 15 cm or 50 cm. The current output was fed into either an Analogic Data 6000 transient recorder or a LeCroy 9450 oscilloscope, where, typically, the current traces from 128 laser shots were averaged.

Reaction intermediates were observed in real time (ns scale) by means of transient absorption spectroscopy. Typically these experiments used the 266-nm output (2.5-ns pulse width) of the YAG system, but, as noted, some studies at 355 nm were performed. The spectrometer detection system consists of a 0.25-m Jarrell-Ash monochromator with 300 and 600 lines/mm gratings and a PAR 1460 optical mutichannel analyzer. The white (probe) light was produced by a 0.5-μs flashlamp. Appropriate optics are employed to collimate and focus the probe beam, and the pump beam is focused into the quartz flow cell with a 15-cm focal length lens. The entire operation—background signal observation, laser and probe lamp intensity meaurements, and transient absorption measurement—is under control of a laboratory microcomputer. Sample solutions were 10^{-4} M in target molecule, and the flow rate through the cell was such that the entire volume was replaced between laser pulses.

Anisole, phenol, and hexane were purchased from Aldrich as 99.99% pure and generally used without further purification. Analyses of these reagents by GC/MS and FTIR spectroscopy confirmed the stated purity. Methanol was purchased from Fisher as UV–liquid chromatography grade and also used without further workup. Distillation of this solvent over drying agents did not affect the observed photoprocesses nor did purification of the hexane by fuming sulfuric acid washing. All gases were purchased from Matheson as Research Grade and used as received.

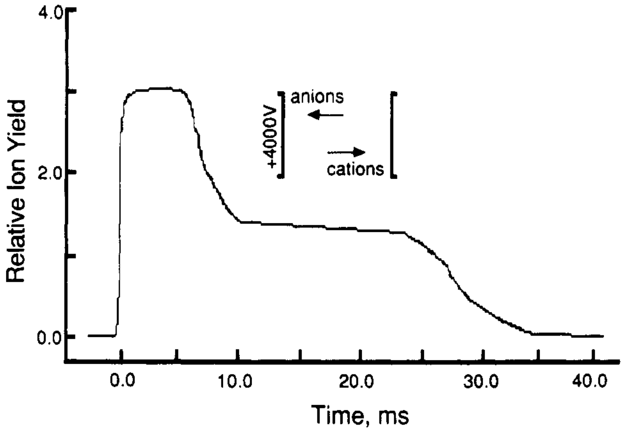

Figure 1. Typical pulsed photoconductivity trace for a 10^{-5} M solution of phenol in hexane. The laser energy was 500 μJ/pulse and the electric field was 6000 V/cm.

Results and Discussion

Three different types of experiments were brought to bear on the study of the multiphoton ionization (MPI) and MPIC of the phenol molecule. Taken as a whole, these experiments present a cohesive picture of the ionization and subsequent kinetics occurring in solution. In this section, the results of the three studies will be separately reported and the discussion, which follows, will draw the connections and eventual conclusions from the data.

Solution Phase Photolysis. It has been previously shown[6] that 266-nm multiphoton-induced chemistry of phenol in hexane leads to production of phenoxyphenol and hexyloxybenzene with quantum yields of 0.022 and 0.026, respectively, at 0.5 mJ/(laser pulse). The laser intensity dependence of these products was shown to increase with I^2, confirming the multiphoton nature of the process and indicating that radical chemistry was not the source of the observed products. Furthermore, the presence of decalin at concentrations of 0.0088 M led to a factor of 2 reduction in the quantum yield for both products. Concentration dependence studies proved that the phenoxyphenol product was second order in the concentration of phenol, while that of hexyloxybenzene was first order in the same reagent. No photochemistry was observed for hexane solutions of phenol when the 355-nm beam was employed as the photolysis source. The qualitative effect of polar solvents on the 266-nm phtochemistry phenol was studied by means of methanolic solutions. Although no quantitative measurements were attempted, analysis of the reaction products indicated only the formation of *o*- and *p*-methoxyphenol.

Pulsed Photoconductivity Measurements. These measurements were made in an attempt to correlate the photolysis results with the observation of ionic precursors. In addition, the liquid TOF technique serves as a means of determining the ionic radius of the active species and, hence, serves as a fingerprinting procedures.[8] A typical photocurrent trace for phenol in hexane is shown in Figure 1. The biphotonic nature of the ion production was confirmed by laser intensity dependence measurements. This is consistent with the photolysis results reported above, and based upon the known electronic structure of phenol may be attributed to a 1+1 REMPI process. Ion yields and the quantum efficiency for ion production were calculated from the time-integrated photocurrent signals, and the results are presented in Table I. The data indicate that even at the highest laser intensities, less than 10^{-5} of the incident photons result in free ions. We estimate, by

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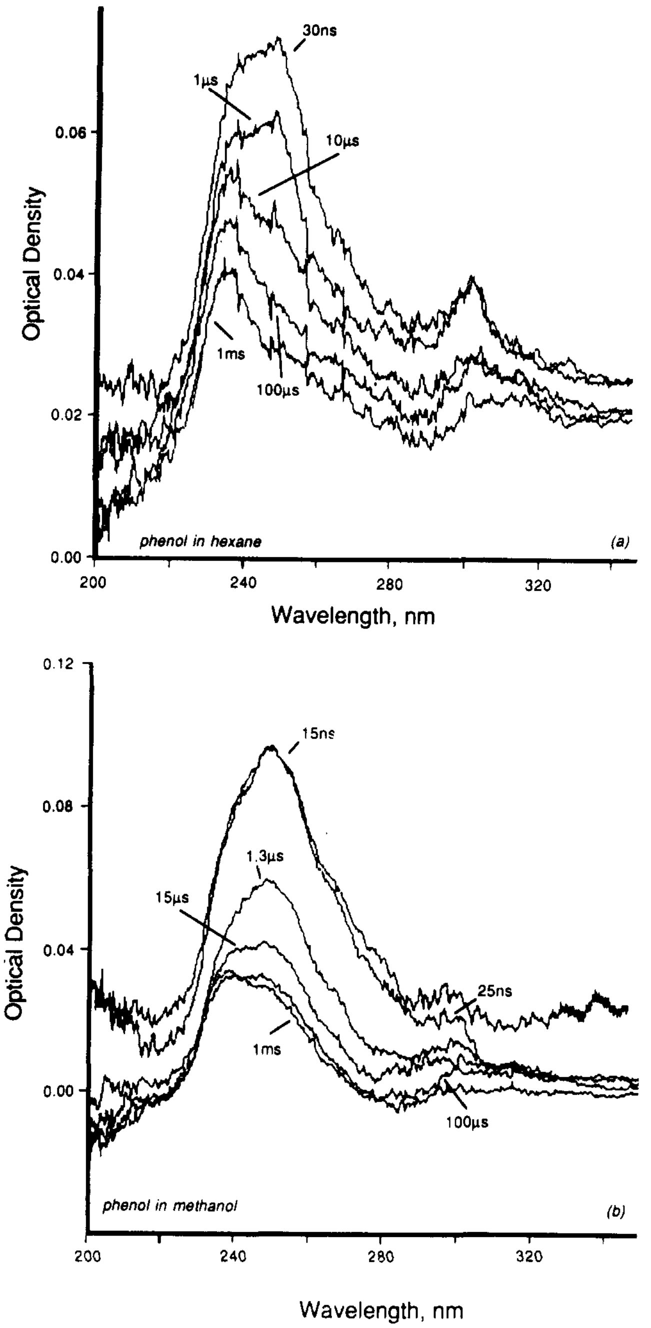

Figure 2. Transient absorption spectra observed after photolysis of 10^{-4} M solutions of phenol in deoxygenated (a) hexane and (b) methanol. The photolysis wavelength was 266 nm and the laser energy was 3 mJ/pulse.

extrapolation, that the absolute quantity of free ions produced for 10^{-5} M solutions *at 500 μJ/pulse* (typical for photocurrent measurements) to be 10^{13} ions/pulse or 0.1%. Further extrapolation to the higher concentrations involved in the photolysis studies (10^{-3} M solutions and 12 000 pulses) leads to an upper limit of 10^{19} ions. Comparison of this total ion production and the number of product molecules formed (10^{16} over the same number of laser pulses) indicates that approximately 0.1% of the free ions created participate in ion–molecule chemistry.

Transient Absorption Spectroscopy. Photolysis of 10^{-4} M solutions of phenol with 2.5-ns pulses at 266 nm (3 mJ/pulse) resulted in intermediates that exhibited absorption maxima at 247 and 300 nm in hexane and 250 and 290 nm in methanol. Similar experiments using neat hexane and neat methanol produced no observable absorption over the wavelength range from 230 to 700 nm. A typical transient absorption spectrum, as a function of the delay time between phtolysis and probing, is shown in Figure 2a for hexane and Figure 2b for methanol. The band at 247 nm is readily assigned to the phenoxy radical as reported in earlier work.[7a,b] The 300-nm feature has not been previously reported, but is assigned to a cationic species on the basis of the following analysis.

TABLE I: Time-Integrated Ion Yield per Pulse as a Function of Laser Energy[a]

energy, μJ/pulse	ion yield, 10^9/pulse	quantum yield of ions, 10^{-5}
5	0.1	1.2
10	0.2	1.3
15	0.6	3.1
20	1.1	4.0
25	1.8	5.4
30	2.6	6.5
35	3.3	7.1
40	4.4	8.2

[a] Ion yield uncertainties average 8%. Phenol concentration is 10^{-5} M.

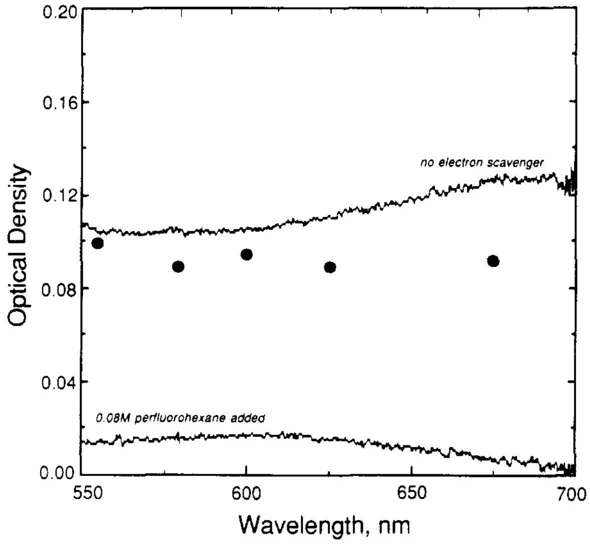

Figure 3. Long-wavelength transient absorption spectrum of phenol in methanol in the presence and absence of the electron scavenger, perfluorohexane (0.8 M). The traces are labeled in the figure. Spectra were recorded for irradiation at 266 nm and 3 mJ/pulse. For comparison purposes, the reported absorption spectrum for the free electron in methanol is shown as the filled circles.[10]

The identical spectrum could be generated in the photolysis of anisole and nitrobenzene, that is, both the 247-nm and 300-nm bands were produced under similar conditions. Moreover, a spectrum with similar features could not be generated in basic aqueous solution but could be formed at pH 3. Previous research has shown that the primary species of basic phenolic solutions is the phenoxy anion, rather than phenol itself.[9] Photoionization of the latter species would yield the phenoxy radical, the spectral features of which are well known and differ from the *new* feature shown in Figure 2. A spectrum similar to that found in the regions of about 300 nm for phenol could be generated (at slightly shifted wavelengths) for acidic solutions. This observation reduces the candidate transient molecules to two: phenol ion and phenoxy ion. The fact that an identical band could be generated via the photolysis of either anisole or phenol (in the same nonaqueous solvents) identifies the transient as the phenoxy cation. The species absorbing at 300 nm showed no reactivity with O_2 or SF_6, confirming that this was not due to a radical.

A longer wavelength spectral region is shown, for methanolic solutions of phenol, in Figure 3. The broad absorption shown is assigned to the spectrum of the solvated electron.[10] As shown in the figure, the absorption at these wavelengths is readily quenched by electron scavengers such as perfluorohexane.

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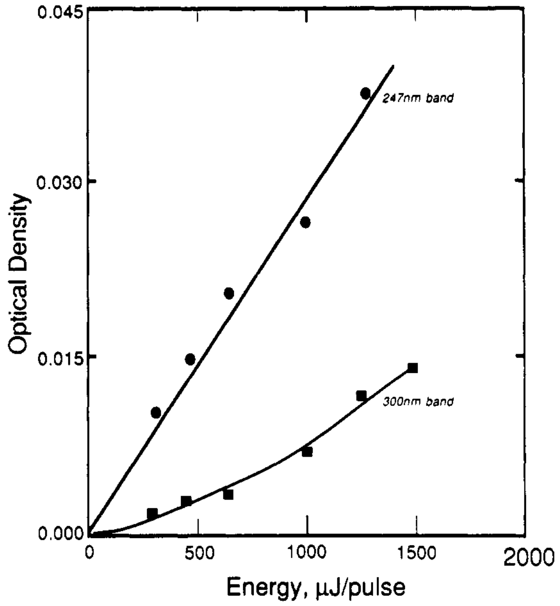


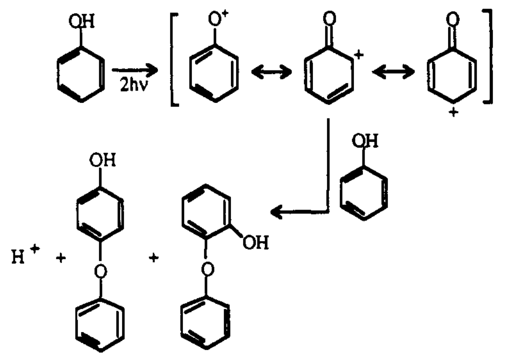
Figure 4. Dependence of radical and cation absorption bands in hexane on laser energy. The least-squares fits are shown and have slopes of 0.9 for the band at 247 nm (circles) and 1.5 for the band at 300 nm (squares).

The extinction coefficient of the cation was determined by using the absorption of the solvated electron as a calibration. In methanol, 30 ns after the laser photolysis pulse, the optical density at 630 nm was 0.11. The extinction coefficient of an electron in methanol is known[11] to be 1.15×10^4 M^{-1} cm^{-1} at this wavelength, yielding an electron concentration of 9.6×10^{-6} M. Given an average optical density for the phenoxycation (at 300 nm) of 0.012, an upper limit for the extinction coefficient is found to be 1.3×10^3 M^{-1} cm^{-1}, assuming a 1:1 correspondence between electrons and cations.

The order of the photoprocess at both 247 and 300 nm was determined by measuring the absorption intensity as a function of incident laser pulse energy (in the range from 300 µJ/pulse to 2 mJ/pulse). The experimental results are shown in Figure 4. A linear relationship was found for the 247-nm band, but the 300-nm band was observed to follow an $I^{3/2}$ dependence, indicating a saturated two-photon ionization process.

Excitation at 266 nm induces a $\pi \rightarrow \pi^*$ transition in phenol.[12] Results described above show that the final fate of the phenol is ionization via a 1+1 REMPI process. Two photons at 266 nm supply 9.3 eV of excitation energy. The ionization potential of gas-phase phenol[13] is 8.5 eV. However, in solution a significant reduction of the ionization potential is observed due to solvation effects.[14] Although the exact magnitude of this reduction is uncertain, previous studies estimate that it is a minimum[14] of 2 eV and has been reported to be as high as 4 eV for phenol.[15] While the latter value seems unreasonably large, 3 eV represents an acceptable compromise between these extremes. The net result is that the phenol radical cation is formed with ~4 eV excess energy. The gas-phase appearance potential[16] for $C_6H_5O^+ + H^\bullet$ is 3.8 eV. Given the amount of excess energy in the radical cation, formation of the phenoxy cation is a possible fate of the 1+1 REMPI-produced ions. This would be consistent with observations in the gas phase that a minimal yield of phenol cation is obtained.[16] A good case may be made on thermodynamic grounds for three-photon production of the phenoxy cation (via 1+1 REMPI followed by ionic absorption); however, this is not directly consistent with our observations. Similarly, one may make a case for the identification of the active ion as the phenol radical cation. Again, this alternative is inconsistent with experimental observations, most especially those experiments involving anisole or nitrobenzene as the target molecule. In those studies using methanol as the solvent, the only products were methoxyphenol and methoxyanisole, which may only be derived from the phenoxy cation as the reactive species. Moreover, the transient absorption spectrum in the case of anisole was identical with that of phenol. All evidence points to the phenoxy cation as the final cationic species.

SCHEME I



The phenoxyphenol photoproducts are attributed to the reaction shown in Scheme I. Similar reactions may be written for hexyloxybenzene and methoxyphenol formation where solvent molecules replace the phenol solute molecule as a reactant in the second step of the reaction. A final confirmation of the importance of the phenoxy cation rather than the phenol radical cation is found in the photochemical experiments involving decalin as a cosolute. Charge exchange with phenol is not possible due to the mismatch of ionization potentials, but decalin is also known to act as a hydrogen atom donor.[17] Such a reaction would regenerate the phenol cation and quench the observed chemistry. This is exactly the observation.

The photoconductivity measurements result in ionic mobilities of the species in solution and may, if sufficiently different, be used to distinguish reactant ions from product ions since the ion mobility is related to the ionic radius via Stokes's Law. In practice, ionic radii were, for the most part, sufficiently similar that such differentiation was not possible. Contributing factors were the relatively small product ion concentration and the possibility of neutral product formation after ion–molecule chemistry. However, the ion mobility measurements did confirm the aryl nature of the cations. The radius of the solvated cation for phenol in hexane was found to be 2.9 Å, which is comparable to the published value[18] for quinine (2.8 Å). Furthermore, the anion was found to have a radius of 2.3 Å, which agrees with the reported value[19] for O_2 in hexane (2.2 Å). Oxygen is the expected anion, even in degassed solutions, since a small, but not negligible, quantity remains. Although the TOF technique did not prove useful in following the course of the reaction, it is further evidence of the nature of the chemistry and indicates that ion–molecule interactions may take place.

The assignment of the two transient absorption bands to different reactive species may also be made on the basis of the disappearance of the absorption band as a function of time in hexane and methanol. In the case of the phenoxy cation, the loss of the signal is attributed, for the most part, to reaction with the solvent or with the parent compound to produce more complex molecules. In the case of the phenoxy radical, the most probable

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fate is hydrogen abstraction from the solvent leading to regeneration of the parent molecule, phenol. The latter path is confirmed by the detection of phenol in the photolysis of anisole. The rate constant for the loss of the cation in methanol was determined to be 2.3×10^5 s^{-1}, and in hexane the same rate constant was measured as 0.8×10^5 s^{-1}. No significant change in these values was observed in the presence of oxygen, even with the use of oxygen as the purge gas during the course of the photolysis. Similar measurements for the decay of the phenoxy radical (spectral feature at 247 nm) were 0.6×10^5 s^{-1} and 1.0×10^5 s^{-1} in hexane and methanol, respectively. All values were for deoxygenated solutions. Measurements of rate constants via the transient absorption spectra are necessarily prone to error and these values should be taken as estimates of the relative rates of radical versus cation reactivity, rather than as absolute values. However, the approximate factor of 3 difference in the rate constants was reproducible and easily observed in the typical transient absorption spectra presented in Figure 2.

To summarize, it has been shown that resonantly enhanced multiphoton pumping of aromatic molecules in solution cleanly produces cationic species, which may then be used as reagents in ion–molecule chemistry. The MPIC technique may be thought of as a more selective type of ionizing radiation and may prove to be a useful technique in probing the nature and rate constants of ion–molecule reactions in solution. Further experimental work will involve the comparison of these solution-phase reactions with gas-phase photochemistry in the presence of the same solvent molecules in order to better characterize the relationship of these gas-phase "solvated" reactant studies to actual studies in solution.

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Charge-Transfer State and Singlet Oxygen ($^1\Delta_g$ O_2) Production in Photoexcited Organic Molecule–Molecular Oxygen Complexes

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We examined charge-transfer (CT) state participation in an excited-state organic molecule (M)–molecular oxygen complex using a variety of time-resolved spectroscopic probes. We showed earlier that singlet oxygen ($^1\Delta_g$ O_2) is formed upon photolysis into the M–O_2 CT absorption band of molecules whose CT state energy is lower than that of the triplet state ($^3M_1$). Our data were consistent with the production of $^1\Delta_g$ O_2 upon dissociation of the photoexcited CT complex. We now examine a molecule whose CT state energy is substantially higher than that of $^3M_1$. Relative $^1\Delta_g$ O_2 and $^3M_1$ yields were determined upon (1) photolysis into the M–O_2 CT band of 1-methylnaphthalene and (2) $^3\Sigma_g^-$ O_2 quenching of triplet 1-methylnaphthalene, which was independently produced. In nonpolar solvents, $^1\Delta_g$ O_2 and $^3M_1$ yields were independent of the *(M–O_2) production method, indicating that relaxation of the ^{1,3}CT states to the $^{1,3}(^3M_1...^3\Sigma_g^-\ O_2)$ states is very efficient. In a polar solvent where the CT state is more stable, the data indicate that *direct* coupling between the CT and ground-state surface $[^3(^1M_0...^3\Sigma_g^-\ O_2]$ may increase. CT-mediated *indirect* coupling of the $^{1,3}(^3M_1...^3\Sigma_g^-\ O_2)$, and other M–$O_2$ excited states, to the ground-state surface should also increase in a polar solvent. $^1\Delta_g$ O_2 quantum yields obtained upon direct photolysis ($^1M_0 \rightarrow {}^1M_1$) of six aromatic hydrocarbons support this interpretation. Our data are consistent with a model for oxygen-induced intersystem crossing in organic molecules in which coupling between singlet and triplet states is facilitated by mixing with a CT state.

Introduction

We are interested in understanding excited-state interactions between molecular oxygen and organic molecules. In an attempt to achieve this goal, we examined (a) ground-state oxygen ($^3\Sigma_g^-$ O_2) induced intersystem crossing in organic molecules (i.e., $^1M_1 \rightarrow {}^3M_1$ and $^3M_1 \rightarrow {}^1M_0$), focusing on the energy-transfer process that results in singlet molecular oxygen ($^1\Delta_g$ O_2),[1,2] and (b) ground-state organic molecule ($^1M_0$) induced deactivation of $^1\Delta_g$ O_2 to $^3\Sigma_g^-$ O_2.[3,4] Continued efforts in this field, however, require a better understanding of the coupling between electronic states of an oxygen–organic molecule complex.

Upon exposure to oxygen, a new feature appears in the absorption spectra of organic molecules. It has been assigned to a transition from a ground-state oxygen ($^3\Sigma_g^-$ O_2)-organic molecule complex to an oxygen-organic molecule charge-transfer (CT) state.[5] The CT state is often represented as a complex with organic molecule radical cation and oxygen radical anion character ($M^{\bullet+}O_2^{\bullet-}$). Theoretical studies indicate that there is significant interaction between the CT state and other states of the M–O_2 complex.[5-8] This is shown in Scheme I in which $^{1,3}(M^{\bullet+}O_2^{\bullet-})$ states mix with the $^{1,3,5}(^3M_1...^3\Sigma_g^-\ O_2)$ states that are formed when $^3\Sigma_g^-$ O_2 quenches a triplet-state organic molecule ($^3M_1$).

This system can also be represented in a model presented by Mulliken[9] in which the wave function for a particular electronic state of the M–O_2 complex can be expressed as a linear combination of zero-order wave functions for all available M–O_2 states (eq 1). The coefficients of expansion (*a*, *b*, *c*, ...) are such that

$$\Psi(M{\cdot}O_2) \simeq a\phi_0(^1M_0,{}^3\Sigma_g^-\ O_2) + b\phi_1(M^{\bullet+}O_2^{\bullet-}) + c\phi_2(^3M_1,{}^3\Sigma_g^-\ O_2) + d\phi_3(^1M_0,{}^1\Delta_g\ O_2) + ... \quad (1)$$

the wave functions (Ψ) for each state (e.g., ground, CT, or locally excited state) are orthogonal to each other. In the ground state, $\Psi(M{\cdot}O_2)$ is dominated by the "no-bond" term ($a \gg b, c, d$). In

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