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MULTIPHOTON IONIZATION OF NITROBENZENE IN NON-AQUEOUS SOLUTIONS: CHARACTERIZATION OF THE CATION AND ION-MOLECULE CHEMISTRY

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(Received 8 January 1991; in final form 25 March 1991)

The phenoxy cation has been generated in polar and nonpolar solutions by multiphoton ionization of nitrobenzene using nanosecond pulses of 266 nm and 355 nm light. The ions have been characterized by pulsed conductivity (ion mobility) measurements and transient absorption spectroscopy. The involvement of the phenoxy ion in ion-molecule chemistry with either neutral solute or solvent molecules has also been observed and the photochemical products and quantum yields of the ion-molecule products are presented and compared with the neutral photochemistry results.

KEY WORDS: Multiphoton induced chemistry, ion-molecule chemistry, multiphoton ionization.

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. In addition, the extensive use of pulsed lasers as initiation sources for photochemical reactions necessitates the improvement of our understanding of the reaction pathways available when a conventional cw source is replaced by high peak power pulses. There is no reason to expect *a priori* that the products or reaction mechanism would be identical in the cw and pulsed initiation modes.

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

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multiphoton techniques for such experiments has not been widely reported. Two-photon absorption leading to ionization has been employed to create geminate pairs for the observation of recombination kinetics and MPI of aromatic solutions has been reported.³ We recently reported two Multiphoton Induced Chemistry (MPIC) studies of aromatic molecules in polar and non-polar solvents,^{4,5} and two other brief communications involving this technique, as applied in other research groups, have appeared.⁶ In these MPIC experiments, the non-linear technique was used to create reactant ions which were then observed to react with both neutral solute and solvent molecules. In this report, we present evidence of the ion-molecule nature of the reaction initiated by MPI by reporting additional photopumping and pulsed conductivity data as well as real-time observations of the cation involved in the reaction. The target molecule, in this instance, is nitrobenzene.

EXPERIMENTAL SECTION

Experiments involving long-term photopumping, 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 third or fourth harmonic crystals and a harmonic separator accessory.

Photopumping studies utilized a specially constructed 5 cm stainless steel cube cell. Full details of the operation of this apparatus have been previously reported,^{4,5} 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 cm³. Irradiation time and laser intensity was wavelength dependent and selected so as to produce a total reactant consumption of approximately 10% or less. For 355 nm ($\tau = 6$ ns, $0.5 \text{ mJ pulse}^{-1} \leq E \leq 15 \text{ mJ pulse}^{-1}$) radiation, one hour exposure, at 10 Hz, resulted in a total irradiation time of 216 μs . At 266 nm ($\tau = 5$ ns, $0.01 \text{ mJ pulse}^{-1} \leq E \leq 10 \text{ mJ pulse}^{-1}$), both one hour and 20 minute exposures were employed resulting in total irradiation periods of either 180 μs or 60 μs . The solutions of nitrobenzene were 0.001 M for 266 nm photolysis, but increased to 0.1 M for the other wavelength due to the decreased absorption cross section. Samples were filtered through micropore syringe filters and gas purged, with N₂, Ar, O₂ or SF₆, as required. Photoproducts were identified and analyzed by quantitative GC/MS using 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 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 8.8×10^{-3} M for the photopumping studies reported here. All quantum yield measurements were made using this photochemical/GC analysis technique and calorimetric determination of the laser energy. The precision of these measurements depends upon the yield of the product, but is typically 5–7%. The exact standard deviations are noted where appropriate.

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 configurations were possible: an opposing pair of 6 mm diameter cylindrical electrodes and a pair of 5 cm by 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 nitrobenzene. The electrode spacing was varied between 1 mm and 5 mm and an applied voltage of 1 kV to 6 kV was routinely applied so that fields of the order of 2 kV/cm to 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 Series 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. 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 Multichannel Analyzer. The white (probe) light is produced from a 0.5 μ s flashlamp. Appropriate optics are employed to collimate and focus the probe beam and the laser, 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 measurements 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. Estimates of the total reaction rate constants were obtained from the transient absorption curves using a point by point analysis of absorption vs. time at 305 nm.

Hexane was purchased from Aldrich as 99.99% pure and generally used without further purification. Nitrobenzene was Electronic Grade as purchased from Kodak Eastman. 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.

RESULTS AND DISCUSSION

The results are summarized by solvent and wavelength so that all applicable data: photochemical, conductivity and transient absorption, are included in each subsection. Subsequently, we construct arguments joining together all of the data and comment on the overall photochemistry and photophysics of the system.

Hexane Solutions with 355 nm (3.5 eV) Radiation

In this instance, the initial absorption is in the wings (extinction coefficient of $\sim 100 \text{ M}^{-1}\text{cm}^{-1}$) of the $n \rightarrow \pi^*$ transition.⁷ Photochemical experiments indicate the production of nitrosobenzene, phenol and hexyloxybenzene with quantum yields (at 8 mJ/pulse) of 0.021 (± 0.001), 0.0053 (± 0.0003) and 0.00048 ($\pm 5 \times 10^{-5}$), respectively. The standard definition of quantum yield is the ratio of product molecules formed to photons absorbed. Since the product formation depends nonlinearly on the number of photons absorbed, this definition is no longer valid. We have chosen to report the quantum yield via the standard calculation, but at a specified laser energy. Clearly, as defined, the quantum yield will vary with changes in the laser pulse energy. Nitrosobenzene has been previously observed for conventional (cw) photopumping at 366 nm, but only in methanolic solution and with a quantum yield which is approximately a factor of three less than that observed in this work.^{7,8} The remaining two products have not been previously reported. The pathway which results in formation of nitrosobenzene is, however, not necessarily identical to that observed at 366 nm. In that study, the decomposition was reported to occur from a triplet state following intersystem crossing from the originally produced singlet. The nitrosobenzene product observed in the current study depends upon the square of the laser intensity, see Figure 1, and nitrosobenzene is a primary and quite stable product. In addition, nitrosobenzene is not observed for a weakly (50 cm focal length lens) focused pump beam nor is the observed product concentration dependent upon the time between production and analysis. The implication is that both dark reactions and monophotonic chemistry are unimportant under the conditions of the experiments. Therefore, two photon excitation would be expected

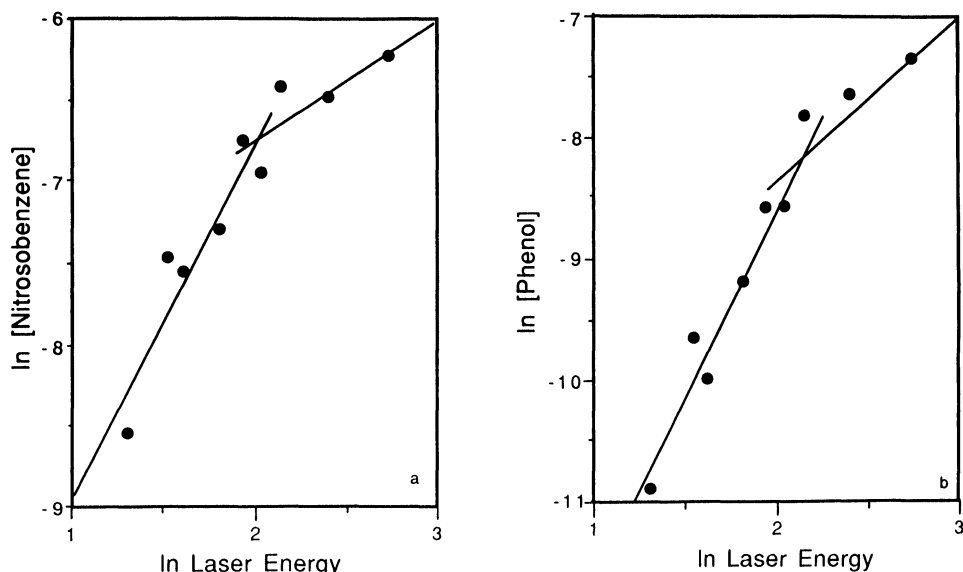


Figure 1 Dependence of the concentration of products in hexane on the laser energy at 355 nm excitation.

to populate a high-lying singlet, which would eventually decay, perhaps after internal conversion to a vibrationally excited ground state molecule, to nitrosobenzene. Moreover, the product yield is identical, within experimental error, whether the solution is saturated with oxygen or deaerated, indicating that a triplet is not involved in the chemistry. Since, a single photon absorbance is known at 355 nm, the likely mechanism for the two-photon excitation to the precursor state is sequential. The high laser intensity results in a rate of absorption in the one photon excited state which is significantly greater than that of intersystem crossing and the transition to the proposed two-photon excited singlet state could become saturated (see below).

The remaining two products depend upon the cube of the laser intensity and are clearly the result of a different, new reaction pathway. The exact nature of this excitation process is not clear, but experimentally, see Figure 1, the three photon dependence is observed, followed by the onset of saturation at higher laser intensities. Consideration of both product dependences on the laser intensity would lead to the conclusion that the mechanism for production of the new photoproducts is also sequential, i.e., the excited state created in the two-photon process is ionized, either by absorption of an additional photon or by autoionization with the additional photon absorbed by the ion.

Pulsed conductivity experiments at this wavelength resulted in the typical trace shown in Figure 2. The portions of the photoconductivity curve corresponding to the

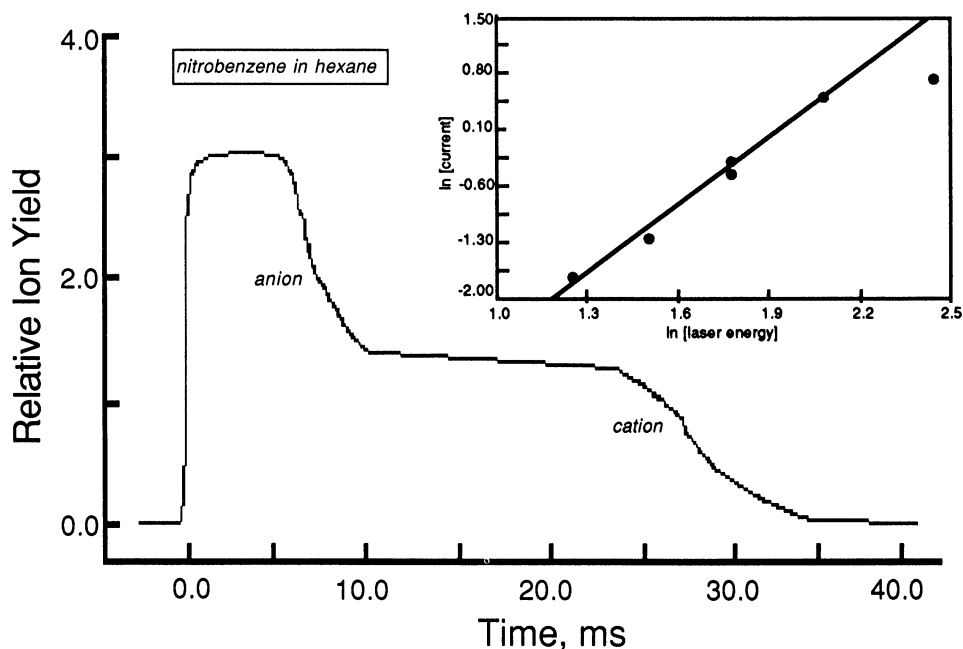
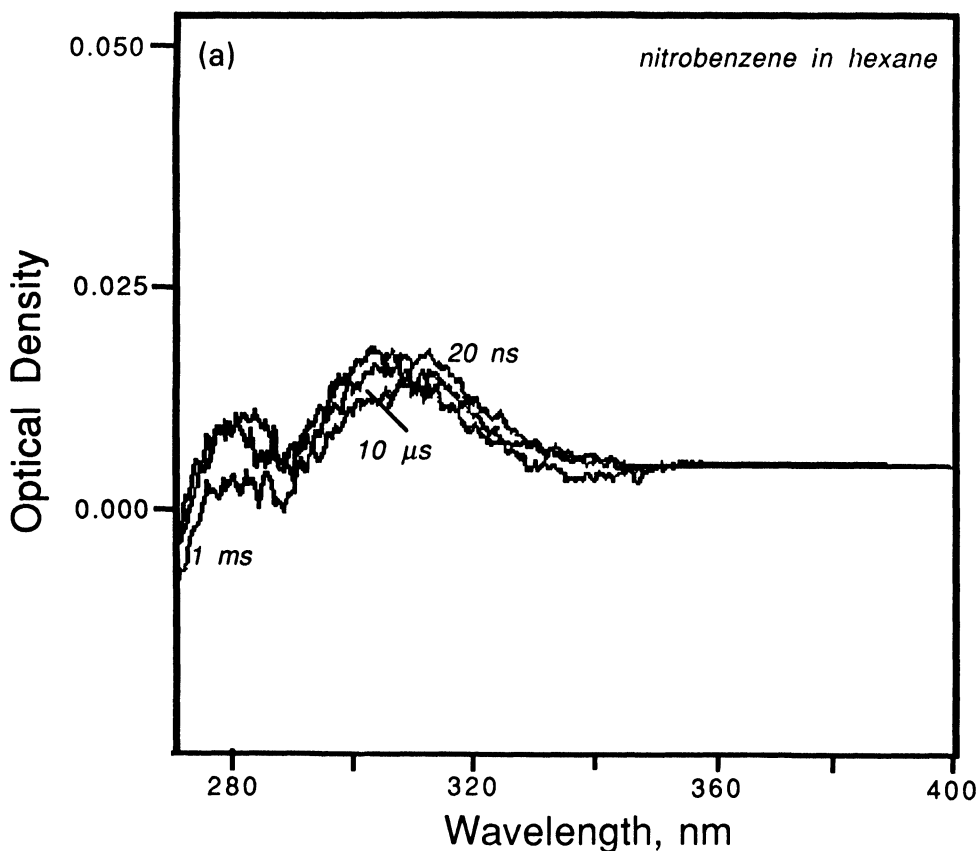


Figure 2 Typical pulsed photoconductivity trace for a 10^{-5} M solution of nitrobenzene in hexane. The laser energy was $500 \mu\text{J/pulse}$ and the electric field was 6000 V/cm . The inset contains several points from the current vs. laser pulse energy determination. The slope of the early points is 2.8, consistent with a three-photon process.

cation and anion were determined by variation of the position of the laser focus between the two electrodes. For example, when the ionization occurs very near to cathode, it is the cations which first arrive at the appropriate electrode since the distance that they must travel is considerably shorter than that of the anions. By reversing the polarity and observing the resulting photoconductivity trace, the assignment may be confirmed. The area of the curve was integrated and a plot of such areas as a function of laser intensity yielded a slope of 2.8, for laser intensities less than or equal to 8 mJ/pulse. Although we have only a single point greater than this value, there appears to be a leveling of the curve shown as the inset in Figure 2, indicating the onset of saturation. These data are consistent with a sequential multiphoton induced process and are further evidence of the ion-molecule nature of the reaction which leads to production of phenol and hexyloxybenzene.

Transient absorption spectra were also recorded in hexane using 355 nm pumping. There are considerable experimental difficulties, since the ground state absorption is so intense at those wavelengths (240–290 nm) that we wish to probe for indications of the presence of the phenoxy radical. These difficulties precluded the possibility of observing a phenoxy radical intermediate in this wavelength range. However, in the



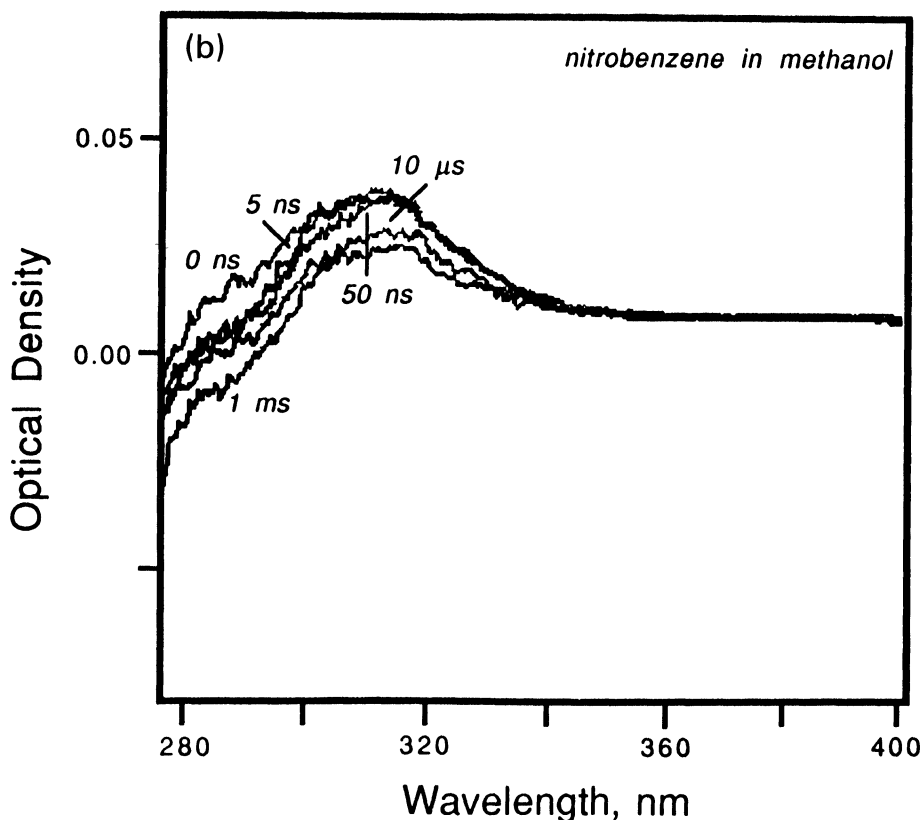


Figure 3 Transient absorption spectra observed after photolysis of 10^{-4} M solutions of nitrobenzene in nitrogen-flushed (a) hexane and (b) methanol. The photolysis wavelength was 355 nm and the laser energy was 3 mJ/pulse.

region about 300 nm, it was possible to observe a weak, but persistent and reproducible absorption which has previously been observed for multiphoton pumping of phenol and anisole and has been attributed to the phenoxy cation.⁵ A series of traces is shown in Figure 3. This is direct evidence for the production of ionic reactants and reinforces our interpretation of the nature of the chemistry which produces the novel photoproducts.

Methanol Solutions with 355 nm (3.5 eV) Radiation

Preliminary photochemical results for this solvent system were reported in an earlier communication.⁴ We have observed the production of nitrosobenzene, phenol and benzyl alcohol, all of which are consistent with the products reported above in the hexane solutions. The corresponding quantum yields at 8 mJ/pulse incident radiation were $0.034 (\pm 0.002)$, $0.0075 (\pm 0.0006)$ and $0.00048 (\pm 4 \times 10^{-5})$, respectively. These measurements involve the same laser energy used in the determination of the

yields in hexane and are consistent with those results. The nitrosobenzene may again be attributed to a neutral photochemical reaction initiated by production of a highly excited state. The small increase in quantum yield over that found in hexane is most likely attributable to triplet formation from the photostate produced by absorption of the first photon in the two-step process. Unlike the hexane solutions, this pathway may make a minor contribution to the production of nitrosobenzene as is evidenced by the approximately 10% decrease in the yield of this product in deaerated solutions as compared with O₂ saturated solutions. Although this change in quantum yield is small, it is outside of the experimental error and is evidence of the additional reaction mechanism. The remaining products were once again shown to depend upon the third power of the laser intensity, indicating the possibility of an ionic precursor as the source of the observed photochemistry.

It is not feasible to conduct photoconductivity measurements in a polar solvent such as methanol. The high electric fields needed to obtain the time-of-flight distribution are sufficiently large so as to promote decomposition of the solvent. Therefore, no conductivity measurements were attempted and this (indirect) method of confirming the presence of an ionic reactant was not available for use.

Transient absorption measurements were completed in this solvent and, in spite of a recurrence of the difficulties reported above for hexane solutions, the absorption in the region about 300 nm was again detected. The existence of a slight solvent shift was also apparent in the results, of which a typical example is shown in Figure 3b. One may draw similar conclusions, as noted above, concerning the existence of an ionic reactant.

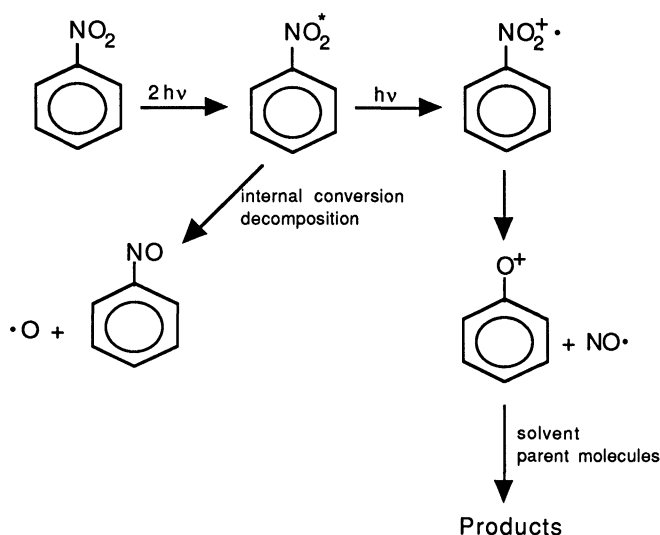
Photochemical Experiments with 266 nm (4.7 eV) Radiation

All three experiments (long term photopumping, pulsed conductivity and transient absorption) were attempted at 266 nm, in both solvents. At this wavelength, the one-photon excitation is $\pi \rightarrow \pi^*$, a transition¹⁰ which exhibits a relatively large absorption cross section. In methanol, no photoproducts were observed and this is attributed to efficient formation of the benzyl radical prior to absorption of a second photon.¹¹ The most likely fate of the benzyl radical is formation of benzene by efficient hydrogen atom abstraction from the solvent and our chromatographic procedure does not readily separate this hydrocarbon from the solvent, although a shoulder in the typical analysis may be due to benzene. Transient absorption spectra did not indicate the presence of either the radical or the cation, indicating that the reaction of the initially created species was faster than the nanosecond time scale of the experiment. In hexane, a similar reaction would be expected and no aromatic product molecules were observed in these photochemical experiments. However, the GC/MS did indicate the formation of alkyl nitrates which were attributed to reaction of the NO₂ radical with the hexane solvent. Photoconductivity measurements confirmed the absence of ion production by the lack of any current signal.

Reaction Mechanism and Kinetics

All of the evidence for 355 nm excitation points to competitive absorption in the

parent molecule leading to branching between neutral and ionic product channels. One of the pathways leads to formation of the nitrosobenzene via neutral bond cleavage, while the other leads to formation of a cation after absorption of additional photons by the initially created excited state. Nitrobenzene has a reported ionization potential of 7 eV in solution.¹² It has already been shown that the yield of the new products depends on the cube of the laser intensity and that the yield of ions, as shown by the conductivity technique, increases with an order nearly equal to three. Given this photophysical data, one concludes that it is the radical cation which is the reactive species or at least the reactive precursor for production of the new products, phenol and hexyloxybenzene. Whether the cation is produced by autoionization following two-photon absorption or three photons are needed to ionize the nitrobenzene, the radical cation would clearly be produced with a large excess energy, ~ 3.5 eV for 355 nm excitation, and fragmentation would be readily possible. Indeed, the phenoxy cation is readily produced by multiphoton ionization in the gas phase. The implication is that, in the liquid as well, the fragmentation results in production of the phenoxy cation and that this is the ion which is involved in the ion-molecule chemistry leading to production of phenol by hydrogen abstraction from the solvent and hexyloxybenzene by reaction with the solvent. Two additional considerations support this conclusion regarding the importance of ionic reactivity: photolysis of nitrobenzene in CCl_4 results in nitrosobenzene formation, but no other products and studies involving the phenylium cation reacting with methane indicate that hydrogen abstraction leading to formation of benzene is significantly favored, by a factor of ~ 20 , over production of toluene.¹³ A simplified version of this reaction mechanism, for 355 nm excitation, is presented below in Scheme 1. Nitrosobenzene has not been previously observed in hexane, has required the presence of oxygen in



Scheme 1 Proposed ion-molecule and radical chemistry for nitrobenzene at 355 nm.

polar solvents and was described as a dark, secondary product resulting from a complicated series of electron transfer steps initiated by the production of phenylhydroxylamine.⁸ It is clear that the excited state which leads to production of the nitrosobenzene at 355 nm is not that previously reported for 366 nm excitation. In the current work, the production of nitrosobenzene depends upon the square of the laser intensity and gas purging studies confirm that the reaction is not due to a triplet precursor. The ease with which the two photon transition becomes saturated indicates that the second step is an allowed transition and that the reaction occurs from a more highly excited state than with 366 nm monophotonic excitation. It is unlikely that the excitation energy remains in the electronically excited molecule, but rather internal conversion and collisional transfer lead to formation of a highly vibrationally excited ground state molecule with subsequent formation of nitrosobenzene. At 266 nm, no photochemistry is observed at all. The absence of any detectable product has been attributed to rapid cleavage of the C-NO₂ bond and subsequent formation of benzene, which cannot be observed in these experiments. This type of photolytic cleavage has been previously reported for nitrobenzene.¹¹

The new and novel reaction products, however, cannot be a result of neutral molecule chemistry and must result from the formation of a cationic species. It is clear that ions are being produced since the pulsed conductivity signals are substantial. Moreover, time-of-flight studies in our conductivity cell yield an ionic radius which is consistent with that previously obtained for phenoxy cations⁵ and similar aromatic molecules. The transient absorption spectrum in the region around 290–310 nm is identical to that previously reported for phenoxy cations generated from phenol and anisole. Finally, the photoproducts observed in this work may be derived from a mechanism nearly identical to that reported for reaction of the phenoxy cation from a phenol precursor in the same solvents.^{5,14}

Estimates of the rate constants for reaction of the cation with the solvent may be obtained from data such as that presented in Figures 3a and 3b. Using the data in figures and additional measurements at the same times, the values for decay of the cation, by all processes, are $3.8 (\pm 1.8) \times 10^4 \text{ s}^{-1}$ and $4.9 (\pm 1.3) \times 10^4 \text{ s}^{-1}$, for hexane and methanol respectively. The rate constants were measured at the absorption maximum (305 nm). Given that the uncertainty in the measurements is estimated to be >20%, the two rate constants are identical. These values are of the same order of magnitude as those reported for loss of the phenoxy cation generated by multiphoton ionization/dissociation of phenol in the same solvents.¹⁴ One important qualitative difference is the apparent lack of ion reactivity with the parent molecule. In the phenol study, the major pathway for decay of the ion, as with many other aromatic ions, was found to be reaction with the neutral parent molecule. The apparent absence of such chemistry for nitrobenzene is rare, but has been observed in other instances.¹⁵

CONCLUSIONS

It has been shown that multiphoton ionization/dissociation may be readily employed to generate cations in solution and that these cations may be used as reagents in

ion-molecule chemistry. Rate constants for the reaction of the phenoxy cation generated from nitrobenzene have been obtained and a competitive kinetic scheme has been proposed to account for the observed neutral molecule and ionic chemistry. The use of multiphoton techniques for generation of reactive ionic species in solution offers considerable advantages over more traditional radiolysis methods. The molecule of interest may be directly ionized without ionization of the solvent molecule and direct methods of observation are readily employed in a small laboratory setting. The use of this type of technique may also find applications in synthesis of novel molecules as well as directly exploring organic reaction pathways which are believed to involve an ionic intermediate.

Acknowledgements

One of the authors (JJB) acknowledges the financial support of the National Science Foundation through Grant Nos. CHE-8521664 and CHE-8852168. The technical assistance of D. Parsons and S. Brown was greatly appreciated.

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