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UV MULTIPHOTON INDUCED CHEMISTRY OF NITROBENZENE IN SOLUTION

JOSEPH J. BELBRUNO†, GARY SIUZDAK and SIMON NORTH‡

Department of Chemistry, Dartmouth College, Hanover, NH 03755 USA

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The technique of Multiphoton Induced Chemistry (MPIC) has been employed to initiate ion-molecule chemistry of organic molecules in solution. We report one of the first examples of the use of liquid phase multiphoton ionization (MPI) to prepare organic cations, which then react with the solvent in ion-molecule processes. The products obtained in this chemical sequence are significantly different from those observed in conventional or multiphoton-induced neutral chemistry in the same solvent. The particular example explored in this work is the reactivity of the nitrobenzene cation in methanol solvent. Products of the ion-molecule chemistry, detected by gas chromatography/mass spectrometry, are phenol and benzyl alcohol. These products depend upon the square of the laser intensity. It is shown by ionization current measurements in a conductance cell, that ionic species are produced as precursors to the observed products. The implications of this application of MPI are briefly discussed. A preliminary report on the unimolecular chemistry of the highly excited neutral molecule is also included. The product of this channel is nitrosobenzene. It is shown, in this case, that the reactive state is most likely a highly vibrationally excited ground state molecule, not the lowest triplet level invoked in conventional photochemistry.

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

INTRODUCTION

The utility of multiphoton ionization as a preparative tool for ion-molecule chemistry in the gas phase has been well-established.[1] However, as suggestive as these results are for reactivity in the condensed phase, the application of the technique to photochemistry in solution has not been widely exploited. We report, in this communication, one of the first examples of organic ion-molecule chemistry initiated by multiphoton ionization in the liquid phase. To our knowledge, only a single other example of such a reaction has been reported, but details in that report were lacking.[2]

The chemical system of interest in this report is nitrobenzene in methanolic solution. The conventional photochemistry of this system at 366 nm has been well-characterized[3,4] and the primary photoproduct in air-saturated solutions is known to be phenylhydroxylamine. The final product depends upon the initial concentration of nitrobenzene and the partial pressure of oxygen, but is either azoxybenzene or nitrosobenzene. The reaction occurs via the lowest triplet level, as confirmed by photolysis of deoxygenated solutions for which the quantum yield for

† Author to whom all correspondence should be sent.
‡ Permanent Address: Department of Chemistry, University of New Hampshire, Durham, NH 03824.

nitrobenzene disappearance is ~30% greater, presumably due to less triplet state quenching. In these latter experiments, nitrosbenzene is not observed, i.e., the source of nitrosobenzene is air oxidation of the primary photoproduct. In the MPIC experiments carried out at 355 nm and reported here, photoproducts from the bimolecular reaction of both a highly excited neutral state of the parent molecule (nitrosobenzene) and a photo-produced radical cation (phenol and benzyl alcohol) were observed. The existence of parallel reaction pathways is confirmed by the different laser intensity dependences of the two products. Careful measurements indicate that the reaction channel leading to the production of nitrosobenzene was not that operative in the conventional photochemistry. Likewise, by means of pulsed photocurrent measurements, we show the presence of solute cations and infer their importance in the MPIC process.

In the following sections, we describe the apparatus and separately discuss the photochemical results and interpretation for both the neutral and ionic reaction channels. The potential utility of the MPIC process in comparison with more traditional solution chemistry methods is also briefly discussed.

EXPERIMENTAL SECTION

The third harmonic of a Nd:YAG laser operated at 10 Hz was focused through a 15 cm focal length lens into a liquid ionization/photolysis cell specifically designed for these experiments. In the ionization mode, the cell volume was approximately 4 cm^3, while a smaller volume of 2 cm^3 was available when the cell was used only for photochemical measurements. Laser energy was in the range from 500 μJ/pulse to 15 mJ/pulse. The cell consisted of a 5 cm stainless steel cube with six ports bored through the cube along perpendicular axes and sealed with quartz windows or stainless steel flanges, as appropriate. Polished stainless steel electrodes could be inserted, with Teflon or Macor insulators, through two of these ports. All window and flange seals were made with either fluorocarbon o-rings or, preferably, with indium gaskets. The cell was isolated in an aluminum box and all connections were made with low noise cabling to minimize rf interference during photoconductance measurements. Several gas purging experiments were carried out and, in these experiments, the gas was passed through the cell containing the reaction mixture for a period of five minutes before sealing the cell. Product identification/quantification was made via gas chromatography/mass spectrometry using dodecane as an internal standard. All photolysis results represent the cumulative effect of 36,000 laser pulses or a total irradiation period of 288 μs. Photolysis experiments were carried out on 0.1 M solutions. At these exposures, a maximum of 5% of the nitrobenzene is reacted, depending upon the laser flux. Photocurrent measurements represent the average of 256 laser pulses and were made with 10^{-5} M solutions. The latter condition was necessitated by the need to avoid, as much as possible, significant absorption outside of the focal region of the excitation pulse.

Nitrobenzene was Electronic Grade from Eastman Kodak Chemicals and the methanol was purchased from Fisher as UV-Liquid Chromatography Grade. These

reagents were used without further purification since analyses by the same techniques used in the experiments indicated that the reagents were pure. The n-hexane was purchased from Aldrich Chemicals (99.99%) and was treated with fuming sulfuric acid, washed with base and dried over molecular sieves prior to use. This treatment resulted in a drastic reduction of the background photocurrent and was necessary even though no impurities were detected by GC/MS. All gases were Research Grade and were obtained from Air Products or Matheson.

RESULTS AND DISCUSSION

Nitrobenzene, in solution, is reported[3] to exhibit weak $n \rightarrow \pi^*$ absorption at 366 nm resulting in photoproduction of nitrosobenzene via a complicated electron transfer scheme originating at the lowest triplet state and involving a number of intermediates. The number of electron transfer steps in the conventional mechanism appeared to be dependent upon both the nature of the solvent (the relative hydrogen donating ability) and the presence of oxygen (a component of dark reactions). In any case, phenylhdroxylamine, the primary photoproduct, could always be detected. The photoproducts observed in the present work depend only upon the laser intensity and do not correlate with any of those observed in the conventional experiments. The neutral and ionic reaction channels are separately discussed below.

Production of Nitrosobenzene

In the current experiments, even at low pulse energies, of the order of 100–800 μJ/pulse, nitrosobenzene could be detected. Nitrosobenzene was not detected when the solution was exposed to the same number of unfocused laser pulses. Moreover, the analysis of the products did not depend upon the length of time between photolysis and analysis. These tests indicate that production of nitrosobenzene by dark reactions and monophotonic processes are relatively unimportant. Production of nitrosobenzene was attributed to a direct process from an excited potential surface of the neutral molecule.[3,4] The rate of production of this molecule appears to be linear (see Figure 1a). However, the best fit line does not pass through the origin. This indicates that the nitrosobenzene is produced through a biphotonic process and one of the steps is saturated.[5] A simple calculation indicates that the saturated step cannot possibly be the initial absorption at 355 nm due to the small extinction coefficient of nitrobenzene ($\sim$100 M^{-1} cm^{-1}) at this wavelength. Therefore, the second step in this sequential two-photon absorption must be saturated. The tendency of this transition to become saturated indicates (but does not definitively assign) this absorption as allowed. The highly excited state created in this process would be short lived in the liquid state and would be expected to rapidly produce the lowest energy singlet or triplet state by nonradiative relaxation or deactivation by solvent collisions. This analysis infers that the reactive state must be a vibrationally hot (probably ground state) molecule. The fact that the second step can be saturated

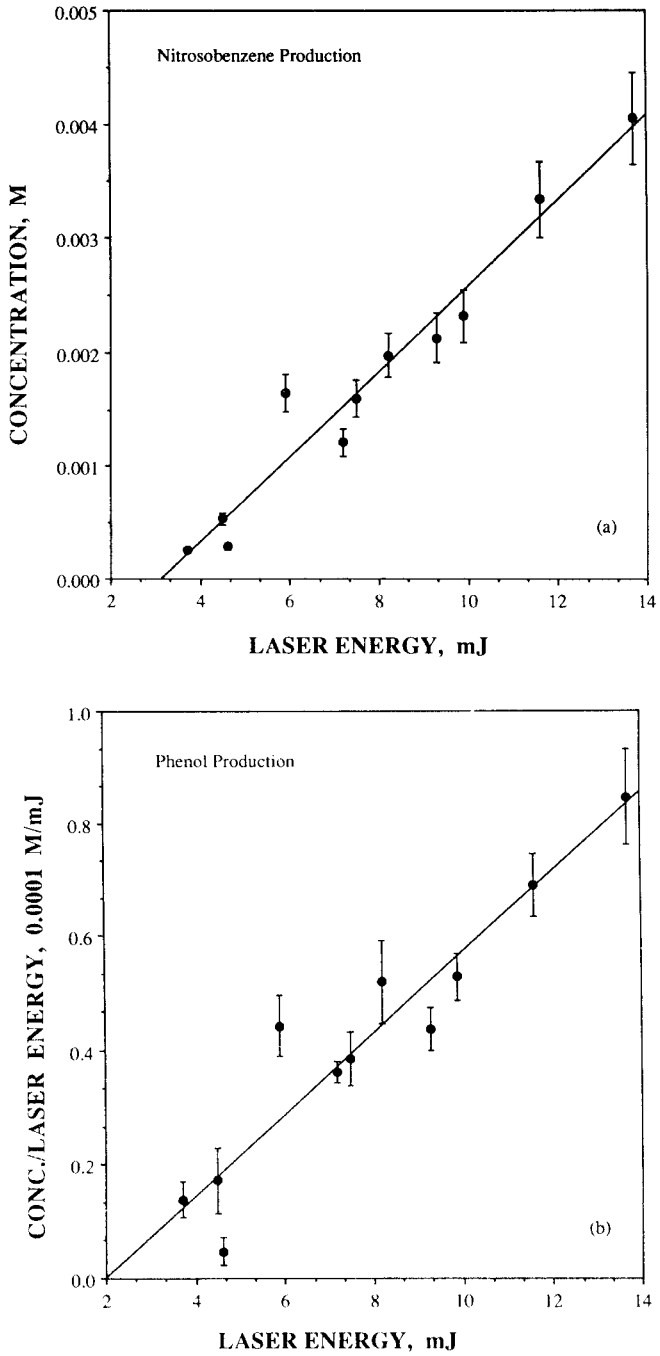

Figure 1 Laser energy dependence of the product yields of nitrosobenzene and phenol for excitation of 0.1 M solutions of nitrobenzene in methanol at 355 nm. The results shown are the cumulative effect of 288 μs exposure (36,000 laser pulses).

indicates that the rate of production of the highly excited precursor state should be sufficiently fast so as to compete successfully with the decay of the initially pumped one-photon level. Unlike the conventional photochemical experiments, nitrosobenzene is produced even in the absence of oxygen. However, samples saturated with SF_6 or Ar yield approximately 10% less nitrosobenzene than those saturated with oxygen or air. No product other than nitrosobenzene may be attributed to the neutral reaction mechanism and we believe that this molecule is a primary photoproduct. The reproducible, but barely statistically significant decrease in yield in the absence of oxygen may be an indication of the extent of the triplet state reaction; however, we have been unable to detect phenylhydroxylamine or the triplet state directly. The quantum yield may also be used to differentiate the multiphoton and conventional experiments. The concept of quantum yield is not directly valid in the context of a multiphoton process due to the nonlinearity, except at a well-defined laser energy. We have chosen to characterize the reaction at 8 mJ/pulse. At this energy we measure $\phi_{\text{Nitrosobenzene}}$, the nitrosobenzene quantum yield, as 3.4×10^{-2}. This is approximately a factor of four greater than that reported in the conventional experiments for the *total* disappearance of nitrobenzene.[3] While most of the mechanistic detail just presented is speculative, it appears clear that the nitrosobenzene produced in this experiment results from a reaction mechanism vastly different from that observed in the traditional experiments.

Production of Phenol and Benzyl Alcohol

Product analysis at the higher laser energies indicated, in addition to nitrosobenzene, the production of benzyl alcohol and phenol. Of the two latter products, phenol is produced in the largest quantity. The quantum yields are $\phi_{\text{Phenol}} = 7.5 \times 10^{-3}$ and $\phi_{\text{Benzyl Alcohol}} = 4.8 \times 10^{-4}$, both at 8 mJ/laser pulse. These additional products do not result from known photochemistry of neutral nitrobenzene.[4,5] Indeed, the rate of production of these products is quadratic in the laser intensity as shown in Figure 1b for phenol. Since at least three photons are required for production and dissociation of the ion, one of the absorption steps (the same step saturated in the production of nitrosobenzene) is again saturated. One might envision the additional reaction channels resulting from processes analogous to those observed in resonantly-enhanced multiphoton ionization in the gas phase.[6] The major species created in the gas phase, either by a stepwise process at 337 nm or resonant two-photon ionization followed by ion absorption at 248 nm, are phenyl ($C_6H_5^+$) and phenoxy ($C_6H_5O^+$) cations. The nitrobenzene radical cation is not observed at all. In the current work, the most likely excitation scheme, as discussed below, is three-photon MPI, but the ion products are expected to be the same as those in the gas phase.[7]

The laser intensity dependence of the reaction pathway in our liquid phase experiments results from the fact that at lower pulse energies the rate constant for dissociation from the initially prepared resonant state is greater than that for absorption of an additional (third) photon leading to ionization, but that the latter process becomes competitive at increased laser intensity. This type of competition between kinetic processes has been observed in the gas phase.[8] The current

knowledge of the spectroscopic states of nitrobenzene is limited and it is not possible to assign the higher energy absorption steps in the MPI process. In any event, the parent ions will contain a substantial amount of excess energy, since three photons at 355 nm yield a total energy of 10.5 eV and the ionization potential of the nitrobenzene molecule is estimated to be approximately 7–8 eV in solution.[9] Gas phase studies have shown that the appearance potential for production of the phenoxy cation is only 1.08 eV greater than the ionization potential of nitrobenzene.[6b] The energy-rich parent *ions* (with an energy 1.5–2.5 ev in excess of that required for extrusion of NO) would be expected to fragment and produce the stable daughter ions noted above.[7] The ions are formed within a solvent cage and proceed to react with surrounding species. The results from the gas saturated liquid samples present additional data with regard to the nature of this reaction. Electron scavengers such as SF_6 and O_2 hinder geminate recombination and stimulate free ion production. One would expect that the presence of a scavenger would increase the yield of ion-molecule products, *if free ions were necessary for reaction*. Instead, whether saturated with O_2, Ar or SF_6, the product yields are identical. The implication is that ion chemistry involving the solvent competes with geminate pair recombination, rather than as a result of reactions with free ions, i.e., the ion-molecule chemistry occurs before the geminate pairs separate, or that the ions are formed with sufficient kinetic energy to readily escape recombination. The range of recombination times covers four decades, 10^{-13} to 10^{-9} s; however, it has been shown in pulsed radiolysis experiments, that certain radical cations may react with solvent molecules, reducing the ion lifetime to the minimum of this time range.[10] The postulated reaction mechanism for phenol production is shown in Scheme 1, where RH is the solvent molecule. An analogous scheme may be constructed for the

$$C_6H_5NO_2 + nh\nu \rightarrow [C_6H_5NO_2{}^{+*} + e^-]\text{solvated} \quad (1)$$

$$[C_6H_5NO_2{}^{+*} + e^-]\text{solvated} \rightarrow [C_6H_5O^+ + e^-]\text{solvated} \quad (2)$$

$$[C_6H_5O^+ + e^-]\text{solvated} \rightarrow [C_6H_5OH + R^+ + e^-]\text{solvated} \quad (3)$$

$$[C_6H_5OH + R^+ + e^-]\text{solvated} \rightarrow C_6H_5OH + R \quad (4)$$

Scheme 1

reaction yielding benzyl alcohol. At the present time, these mechanisms are somewhat speculative, but they are consistent with all of the experimental observations. The rate of Reaction (2) has been measured in the gas phase.[11] The reported value, $6 \times 10^5\ s^{-1}$, is much too slow to compete effectively with geminate recombination. One must, therefore, assume that the thermalization distance is indeed sufficiently large so as to limit recombination and permit the photochemistry to be observed on the millisecond timescale of the experiments. If the thermodynamics of Reactions (3) and (4) are carefully examined, one finds that the data are consistent with the proposed mechanism. In particular, the hydrogen affinity of $C_6H_5O^+$ is greater[12] than that of R^+ (3.8 eV vs. 0.4 ev)[13], so that the hydrogen transfer is readily facilitated.

Although the results of the SF_6 saturated experiments indicate that the product is not expected to correlate with the quantity of free ions, an attempt was made to compare the ion current with phenol production to directly determine the importance of *free* ions and to assess the magnitude and laser intensity dependence of ion production. Unfortunately, polar solvents are not suitable for the pulsed conductivity measurements needed to record the MPI current. It is possible, however, to record the ion current in non-polar solutions and time-dependent MPI induced current measurements were conducted for 1×10^{-5} M solutions of nitrobenzene in n-hexane. Figure 2 shows a typical trace, as well as the increase in ion production with increasing laser intensity. As in the instance of phenol and benzyl alcohol product formation, the ion yield is second order in the number of photons present. These experiments are an indication of the presence of reactive ionic species, albeit in another, poorer, solvent. A more direct comparison will be made in future measurements of the same MPI-driven reaction using hexane as the solvent. Preliminary measurements indicated that hydrogen abstraction by the $C_6H_5O^+$ ion from the solvent was occurring even with as poor a hydrogen donor as hexane. This type of reaction in non-polar solvents does not occur for the neutral photochemistry of nitrobenzene[3,4] and is further evidence of the ion-molecule nature of the reaction under study. More extensive experiments utilizing hexane are underway and will be reported in a future publication.

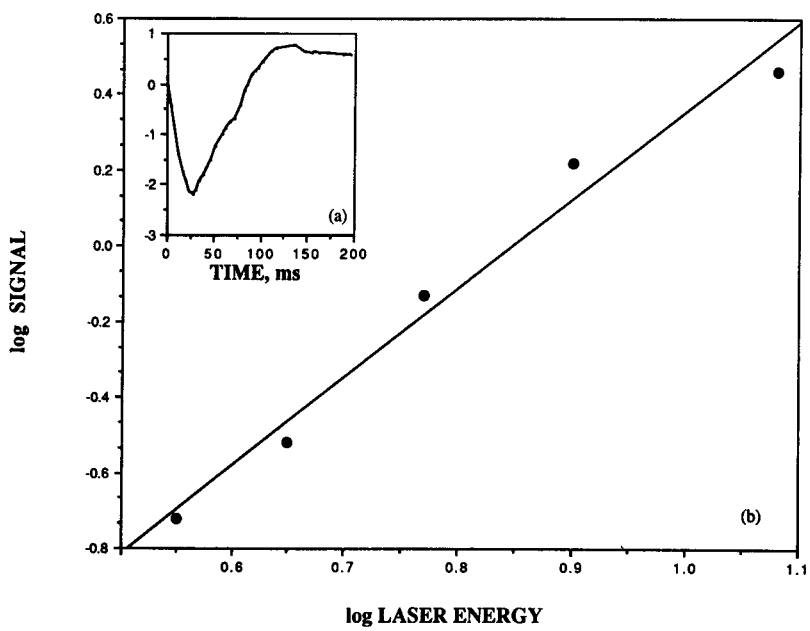

Figure 2 (a) Time dependence of the multiphoton ionization current for a 10^{-5} M solution of nitrobenzene in n-hexane. The trace shown represents the average over 256 laser pulses at an applied field of 9 kV/cm. The rise immediately following the detected current pulse is an experimental artifact due to the coupling capacitance. (b) The laser pulse energy dependence of the signal intensity. The slope of the least squares fit shown in the figure is 1.9.

Potential Utility of MPIC

These experiments have implications in two very different fields. The production of reactant ions via MPI is considerably more selective than production of the same reactants by pulse radiolysis. Use of MPI would permit the assignment of the reactive species in some experiments for which the electron bombardment has created a wide variety of reactive species any one of which may be a participant in the ion-molecule chemistry.[14] The method may also have synthetic applications and lead to the synthesis of new products through novel ion, rather than neutral photochemistry. Evidence of such reactivity has already been reported in the gas phase.[1(a),8]

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