

Resonant ionization in solution: Initiation of ion-molecule chemistry by REMPI

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ABSTRACT: REMPI is employed to create ions in solution. The radical cations are then involved in ion-molecule chemistry with the solvent or added co-solutes. The formation of the ion is confirmed by pulsed conductivity measurements and transient absorption spectroscopy. Long-term photochemical products are also identified. The ion kinetics and a likely reaction mechanism are presented.

1. INTRODUCTION

Considerable research effort has been concentrated on determining the effects of ionizing radiation on organic solutions. Typically in radiation chemistry, an electron beam interacts with the solvent, so that the observed reactions involve a large quantity of reactive solvent molecules interacting with a much smaller concentration of neutral solute molecules. The technique described in this report overcomes this limitation of conventional radiation chemistry. Multiphoton induced ion-molecule chemistry is initiated by the creation of reactive *solute* species, that is, the selectivity of the REMPI technique permits ionization of the species of interest, rather than that present in the greatest amount. In this report, we describe our initial results (BelBruno, et al., 1990a, 1990b) applying this technique to phenol and nitrobenzene in polar and non-polar solvents.

2. EXPERIMENTAL

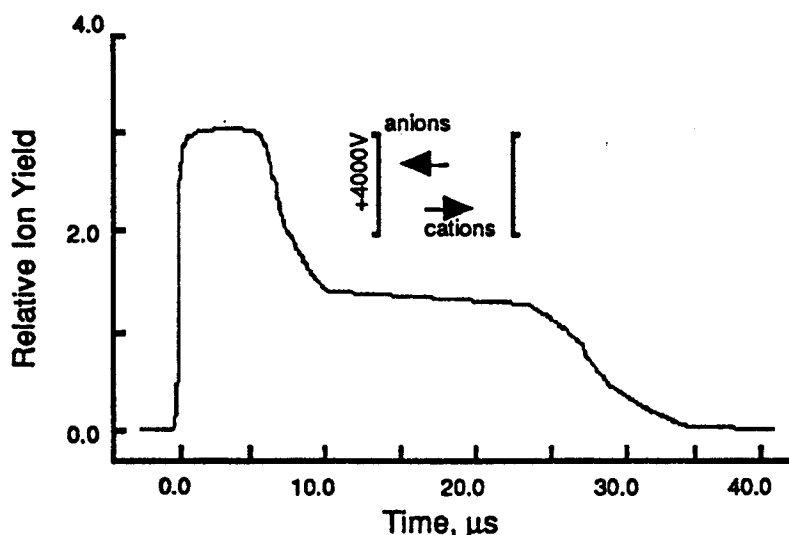
Experiments involving long-term photo-pumping, pulsed conductivity measurements and transient absorption spectroscopy were conducted. In all cases, the light source was a Quanta Ray DCR11 Nd: YAG laser with appropriate third or fourth harmonic crystals. Photo-pumping studies utilized a specially constructed 2 cm³ stainless steel cube cell. Irradiation time and laser intensity were selected so as to produce a reactant consumption of 10% or less. The solutions of phenol were 0.001M, but increased to 0.1M for nitrobenzene. The pulsed conductivity measurements a modified version of the same stainless steel cell. Routine measurements involved solutions of 10⁻⁵M and fields of the order of 2kV/cm to 10kV/cm. Reaction intermediates were observed in real time (ns scale) by means of transient absorption spectroscopy. The spectrometer consists of a 0.25m monochromator and an optical multichannel analyzer. The probe flash is produced by a 0.5 ms flashlamp. Sample solutions were 10⁻⁴M in target molecule and the flow rate through the cell was such that the entire volume was replaced between flashes.

3. RESULTS

No ionization or ion-molecule chemistry was observed for irradiation of phenol at 355nm or nitrobenzene at 266nm. For nitrobenzene, the excitation of the $\pi \rightarrow \pi^*$ transition was presumed to efficiently produce the benzyl radical, while for phenol the coherent two-photon absorption at 355nm produces radicals with subsequent recombination.

At 355nm the initial absorption for nitrobenzene in hexane is in the wings ($\epsilon \approx 100 \text{ M}^{-1}\text{cm}^{-1}$) of the $n \rightarrow \pi^*$ transition. Photochemical experiments indicate the production of nitrosobenzene, phenol and hexyloxybenzene with quantum yields (at 8mJ/pulse) of 0.021, 0.0053 and 0.00048, respectively. The nitrosobenzene observed in the current study depends upon the

Figure 1. Pulsed conductivity of nitrobenzene in hexane.



square of the laser intensity and is a primary product. No products are observed for the weakly (50cm focal length lens) focused pump beam nor is the observed product concentration dependent upon the time between production and analysis. Dark reactions and monophotonic chemistry are unimportant under the conditions of the experiments. Two-photon excitation would be expected to populate a high-lying singlet of the neutral molecule, which would decay, after internal conversion to a vibrationally excited ground state molecule, to nitrosobenzene. Since, a one-photon absorbance is known at 355nm, the likely mechanism for the two-photon excitation to the precursor state is sequential. The remaining two products depend upon the cube of the laser intensity and the mechanism for production of these products is also sequential. Pulsed conductivity experiments at this wavelength resulted in the typical trace shown in Figure 1. A plot of the area under the curve vs. laser intensity yields a quadratic dependence, indicating that the intensity regime probed was intermediate between that of a totally saturated process and the unsaturated (power dependence of 3) pathway. 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 phenol and hexyloxybenzene. Transient absorption spectra were recorded. There are considerable experimental difficulties, since the ground state absorption is so intense in the 240-290nm range. However, in the region about 300nm, it was possible to observe a weak, but reproducible absorption, which has previously been attributed to the phenoxy cation. This is direct evidence for the production of ionic reactants.

Preliminary photochemical results for the methanolic system were reported in an earlier communication (BelBruno, et al., 1990a). 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, 0.0075 and 0.00048, respectively. These yields are consistent with those found in hexane. The nitrosobenzene may again be attributed to a neutral photochemical reaction initiated by production of a highly excited singlet state. The small increase in quantum yield over that found in hexane is attributable to triplet formation from the photostate produced by absorption of the first photon in the two-step process. The remaining products were shown to depend upon the cube of the laser intensity, indicating an ionic precursor for the observed photochemistry. Transient absorption measurements detected the cation absorption in the region about 300nm.

It has been previously shown that 266nm multiphoton induced chemistry of phenol in hexane leads to phenoxyphenol and hexyloxybenzene with quantum yields of 0.022 and 0.026 at 0.5mJ/pulse. The laser intensity dependence of these products was shown to be I^2 ,

confirming the multiphoton nature of the process and indicating that radical chemistry was not the source of the observed products. The qualitative effect of polar solvents on the 266nm photochemistry of phenol was studied by means of methanolic solutions. Although no quantitative measurements were attempted, analysis of the products indicated only the formation of o- and p-methoxyphenol. Concentration dependence studies proved that the

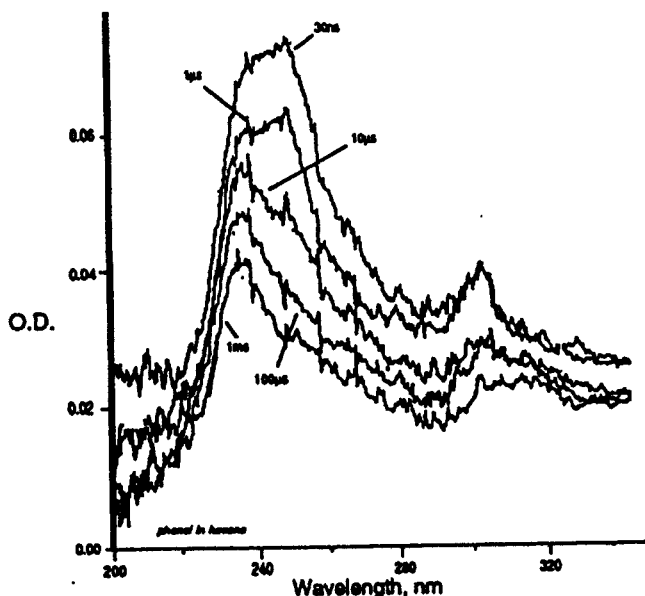


Figure 2. Transient absorption spectra of phenol in hexane

probing, is shown in Figure 2 for hexane. The band at 247nm is readily assigned to the phenoxy radical. The 300nm feature has not been previously reported, but is assigned to a cationic species.

Longer wavelength transient data for methanolic solutions of phenol are assigned to the spectrum of the solvated electron. The absorption at these wavelengths is readily quenched by electron scavengers. The extinction coefficient of the cation was determined using the absorption of the solvated electron as a calibration. In methanol, 30ns after the laser photolysis pulse, the optical density at 630nm was 0.11. The extinction coefficient of an electron in methanol is known to be $1.15 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ yielding an electron concentration of $9.6 \times 10^{-6} \text{ M}$. Given an optical density for the phenoxy cation (at 300nm) of 0.012, an upper limit for the extinction coefficient is found to be $1.3 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$ assuming a 1:1 correspondence between electrons and cations. The order of the photoprocess at both 247nm and 300nm was determined by measuring the absorption intensity vs. laser pulse energy. A linear relationship was found for the 247nm band, but the 300nm band was observed to follow an $I^{3/2}$ dependence indicating a saturated two-photon ionization process.

4. DISCUSSION

In nitrobenzene, all of the evidence points to competitive absorption in the parent molecule leading to branching between neutral and ionic product channels. One pathway leads to nitrosobenzene via neutral bond cleavage, while the other leads to formation of the phenoxy cation after absorption of additional photons by the initially created radical cation. A total of three photons is necessary to ionize nitrobenzene which has a reported ionization potential of 7 eV in solution. Given this data, one concludes that it is the radical cation which is the reactive precursor for production of the new products, phenol and hexyloxybenzene. The radical cation would clearly be produced with a large excess energy, $\sim 3.5 \text{ eV}$, and fragmentation would be readily possible. The phenoxy cation is readily produced by MPI in the gas phase. The implication is that, in the liquid as well, fragmentation results in production of the phenoxy cation and that this is the ion involved in the ion-molecule chemistry leading to

phenoxyphenol product was second order in the concentration of phenol, while that of hexyloxybenzene was first order in the same reagent. Ion yields from pulsed photoconductivity measurements and the quantum efficiency indicate that less than 10^{-5} of the incident photons result in free ions. We estimate by extrapolation, that the absolute quantity of free ions produced at $500 \mu\text{J/pulse}$ and 10^{-5} M solutions to be 10^{13} ions/pulse or 0.1%. Calculations also indicate that of these free ions only approximately 0.1% participate in ion-molecule chemistry. Photolysis of 10^{-4} M solutions of phenol with 2.5ns pulses at 266nm resulted in intermediates which exhibited absorption maxima at 247nm and 300nm in hexane and 250nm and 290nm in methanol. Typical transient data, as a function of the delay time between photolysis and

production of phenol, by hydrogen abstraction from the solvent, and hexyloxybenzene, by reaction with the solvent. Two additional considerations support this conclusion: 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. Rate constants for the cation with the solvent are obtained from data in Figure 2. The values for decay of the cation, by all processes, are $5.4 \times 10^2 \text{s}^{-1}$ and $5.0 \times 10^2 \text{s}^{-1}$, for methanol and hexane. Given that the uncertainty in these measurements is estimated to be 20%, the two rate constants are identical. The small rate constant may be attributed to the apparent lack of ion reactivity with the parent molecule.

For phenol, results show that the final fate is ionization via a 1+1 REMPI process. Two photons at 266nm supply 9.3eV of excitation energy. The ionization potential of gas phase phenol is 8.5eV; however, in solution previous studies have shown that it is reduced by a minimum of 2eV, and perhaps as much as 4eV. The net result is that the phenol radical cation is formed with $\sim 4\text{eV}$ excess energy. The gas phase appearance potential for $\text{C}_6\text{H}_5\text{O}^+$ and H^\bullet is 3.8eV. Given the amount of excess energy in the radical cation, formation of the phenoxy cation is the probable fate of the 1+1 REMPI produced ions. A good case may be made on thermodynamic grounds for three-photon production of the phenoxy cation; however, this is inconsistent with our observations. Similarly, one may make a case for the active ion being the phenol radical cation. Again, this alternative is inconsistent with experimental observations, most especially those experiments involving anisole as the target molecule. In those studies using methanol as the solvent, the only products were methoxy phenol and methoxy anisole. These may only be derived from the phenoxy cation. All evidence points to the phenoxy cation as the final cationic species. The photoproducts are attributed to reactions of this cation with neutral phenol molecules or solvent.

The assignment of the two transient 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 to reaction with the solvent or the parent compound. In the case of the phenoxy radical, the most probable fate is hydrogen abstraction from the solvent leading to regeneration of the parent molecule, phenol. This 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 $2.3 \times 10^5 \text{s}^{-1}$ and in hexane the same rate constant was measured as $0.8 \times 10^5 \text{s}^{-1}$. Similar measurements for the decay of the phenoxy radical (spectral feature at 247nm) were $0.6 \times 10^5 \text{s}^{-1}$ and $1.0 \times 10^5 \text{s}^{-1}$ in hexane and methanol, respectively. 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 absolute values. However, the approximate factor of 3 difference in the rate constant was reproducible.

Finally, the conductivity measurements may be used in a time-of-flight mode. The measurements yield ionic mobilities and may, if sufficiently different, be used to distinguish reactant ions from product ions. The radius of the solvated cation for phenol in hexane was found to be 2.9Å, which is comparable to that for quinine (2.8Å). Furthermore, the anion was found to have a radius of 2.3Å which agrees with that for O_2^- in hexane (2.2Å). Oxygen is the expected anion, even in degassed solutions, since a small, but not negligible, quantity remains.

5. REFERENCES

- BelBruno J J, Siuzdak G and North S 1990a, *Laser Chem.* **10**, 177
BelBruno J J, Siuzdak G and North S 1990b, *Chem. Phys. Lett.* **166**, 167