MULTIPHOTON-INDUCED CHEMISTRY OF PHENOL IN HEXANE AT 266 nm

Joseph J. BELBRUNO [1], Gary SIUZDAK and Simon NORTH [2]

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

The technique of multiphoton-induced chemistry (MPIC) has been employed to initiate ion–molecule chemistry of phenol in *n*-hexane solution. The technique involves the use of liquid phase multiphoton ionization (MPI) to prepare organic cations, which then react with the solvent in ion–molecule processes. Products of the ion–molecule chemistry, detected by gas chromatography/mass spectroscopy, are phenoxyphenol and hexyloxybenzene. These products depend upon the square of the laser intensity. It is explicitly shown by pulsed ionization–current measurements, that ionic species are produced as precursors to the observed products. Moreover, positive ion scavengers inhibit the reactivity. Estimates of the rates and quantum yields for the title process are given, as are rate data for the inhibition of the reaction by the ion scavenger, decalin. A brief discussion of the mechanism is also presented.

1. 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 two other examples of such a reaction have been reported and one of those reports was of our earlier MPIC work with nitrobenzene in methanol [2,3].

The use of pulse radiolysis to initiate radical and anion/cation chemistry in the liquid phase is well-established. In radiation chemistry techniques, the electron beam interacts mainly 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 [4]. This inherent indiscriminate ionization/excitation

may been overcome, to some extent and under particular circumstances, by various electron or excitation transfer processes, but the presence of a large and varied number of potential reactants is unavoidable. The technique described in this report overcomes this limitation radiation chemistry. MPIC ion–molecule chemistry is initiated by the creation of reactive *solute* species. The availability of high resolution lasers and the development of techniques such as resonantly enhanced multiphoton ionization permit the selective excitation of the target molecule, while the solvent remains transparent. The inherent advantages of the selectivity offered by this technique are obvious. The reactive cation may be the initially prepared molecule or a decay product of that reactant. In this regard, the usual spectroscopic details of the solute must be known in advance; however, that information is required for successful application of almost any kinetic technique. The reactant of interest is then allowed to interact with either solvent molecules or a co-solute. Reaction with the solvent cage about the solute merely requires the generation of geminate pairs, since the ready availability of the solvent as a reaction partner may effectively compete with geminate pair recombination. However, the initiation of a reaction with a co-solute present in relatively small quantities will nor-

---

[1] To whom correspondence should be addressed.
[2] Permanent address: Department of Chemistry, University of New Hampshire, Durham, NH 03824, USA.

mally require the assisted generation of free ions either by application of an electric field to the photolysis cell or by separation of the geminate pair via chemical means. This report details the application of this technique to solutions of phenol in n-hexane. In the MPIC experiments carried out at 266 nm and reported here, photoproducts from the bimolecular reaction of a photo-produced radical cation with both neutral solvent and solute molecules were observed. The existence of the new reaction pathways is confirmed by the laser intensity dependences of the two products. By means of pulsed photocurrent measurements, we show the presence of solute cations and infer their importance in the MPIC process. A reaction mechanism initiated by means of a two-photon (1 + 1) ionization process is consistent with the observations. A significant fraction of the original solute molecules are converted into photoproducts by this process. The utility of MPIC as well as a brief comparison of the technique with the more traditional electron beam methods are also discussed.

2. Experimental

The fourth harmonic of a Nd:YAG laser operated at 10 Hz (pulse length 6 ns, or in some instances, 2.5 ns) 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 cm³, while a smaller volume of 2 cm³ was available when the cell was used only for photochemical measurements. Laser energy was restricted to the range from 100 μJ/pulse to 1 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 with a variable separation. The actual electrode separation was determined by optical microscopy. All window and flange seals were made with fluorocarbon O-rings. Gas purging experiments utilizing SF_6, O_2 and Ar were carried out and, in these experiments, the gas was allowed to pass through the cell containing the reaction mixture for a period of five minutes before sealing the cell. These experi-

ments were intended to test the effects of elect scavenging on product formation. Product iden cation/quantification was made via gas chroma raphy/mass spectrometry using dodecane as an ternal standard. Most photolysis results represent cumulative effect of 12000 laser pulses (at 6 n pulse) or a total irradiation period of 72 μs and exceptions are noted in the text. Standard exp ments were carried out on 0.001 M solutions. viations from this norm are also appropriately n At these exposures, a maximum of ≈ 10% o phenol is reacted, depending upon the laser Photocurrent measurements represent the avera 128 laser pulses using concentrations identica those employed in photolysis. The concentration dictated by the large absorption coefficient of ph in this spectral region and the need to avoid, as m as possible, significant absorption outside of th cal region of the excitation pulse.

Phenol and n-hexane were purchased from drich (as 99.99% pure). Analyses by the same niques used in the experiments indicated that th agents used were pure. The n-hexane has an inhe conductivity which may overwhelm the signal a tain frequencies; however, this background i significant with phenol as the solute and the length set to 266 nm. Numerous methods fo moving impurities were pursued, but in the ca the particular solvent chosen for the study, th herent ionization current could be further redu All gases were Research Grade and were obta from Air Products or Matheson.

3. Results and discussion

The photophysics of phenol in the spectral re about 266 nm are well-known [5]. The radiatio duces a $\pi \rightarrow \pi^*$ transition ($\sigma_{266\,nm} = 2.4 \times 10^{-18}$ c As with most simple substituted benzenes, this e tronic state is stable with respect to photodisso tion and is expected to relax by non-radiative t sitions to high vibrational levels of the gro electronic state. Under irradiation by the high tensities ($\approx 5 \times 10^7$ W cm⁻²) employed in this stu the (electronically or vibrationally) excited ph molecule absorbs an additional photon and is ized. Two photons of wavelength 266 nm supply

eV of excitation energy to phenol. The gas phase ionization potential is reported [6] to be 8.5 eV. The ionization potential of a molecule in a non-polar solvent is lowered by at least 2 eV due to solvation of the ion and electron [7]. In the case of phenol, this effect has been reported to be 4 eV, so that the ionization potential in hexane solution could be as low as 4.5 eV [8]; however, this appears to be an overestimation of the magnitude of the solvation effect. In general, the two-photon excited phenol has ≈ 3 eV more energy than is required for ionization and easily accesses the ionization continuum, even with rapid dissipative processes in competition. The appearance potential for the fragments [9], $C_6H_5O^+$ and H, is 3.8 eV, and the fragmentation process should not readily occur at the two-photon excitation level. In the gas phase [9], multiphoton ionization mass spectra indicated considerable fragmentation of the parent phenol ion to produce $C_6H_5O^+$, $C_5H_6^+$ and $C_3H_3^+$, but the fragmentation channels were energy dependent and the relative quantities of these products were laser frequency dependent. Based on the known thermodynamics and the gas phase results, scission of the O–H bond in the phenol cation should not be observed until a total of three photons are absorbed.

$$
\text{(I)} \qquad \text{(II)}
$$
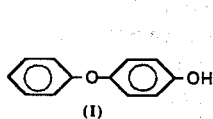
Production of phenoxyphenol and hexyloxybenzene. Product analysis by quantitative GC/MS using an internal standard indicated the production of phenoxyphenol (I) and hexyloxybenzene (II). The quantum yields are $\Phi_{phenoxyphenol} = 2.2 \times 10^{-3}$ and $\Phi_{hexyloxybenzene} = 2.6 \times 10^{-3}$, both at 0.5 mJ/laser pulse. The specification of a particular laser energy and the use of identical beam and focusing conditions is essential, since the non-linearity of the ionization process distorts the usual meaning of the quantum yield. The G value, typically used in radiation chemistry and defined as the number of molecules changed per 100 eV of energy absorbed, may be more useful than quantum yield. For the products observed in this reaction, G(phenoxyphenol) = 0.048 and G(hexyloxybenzene) = 0.055, both results are per 100 eV input energy. These products do not result

from any known linear photochemistry of pheno [8]. Indeed, the rate of production of these product; is quadratic in the laser intensity as shown in fig. 1 The lines; however, do not pass through the origin Previous research has shown that the presence of a non-zero intercept may indicate that the process under observation results from absorption of at least one photon more than is indicated by the slope ol the best fit line [10]. The inference is that the chemical yields are actually a result of a three-photon process and it has already been shown that this level of excitation may lead to formation of the phenoxy cation. The spectroscopic understanding of the low lying states of phenol is excellent and it is a simple matter
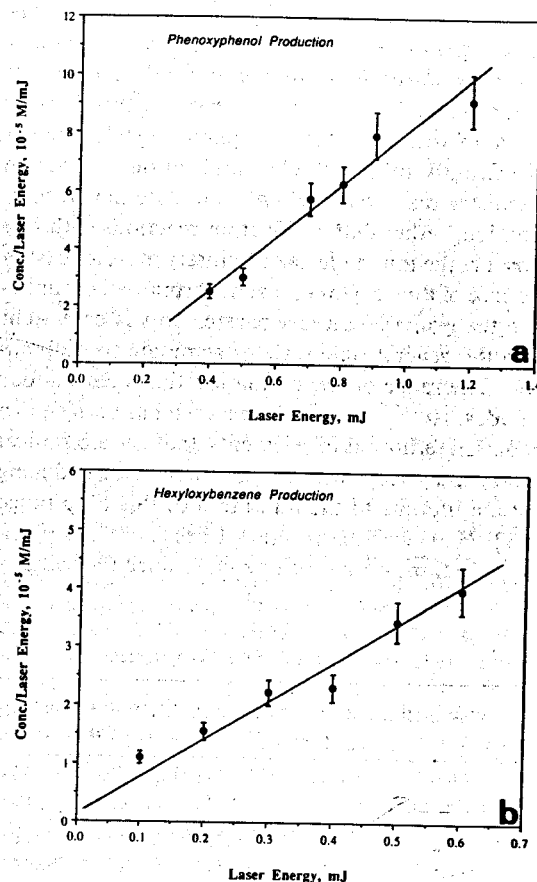

Fig. 1. Laser energy dependence of the product yields of phenoxyphenol and hexyloxybenzene for excitation of 0.001 M solutions of phenol in n-hexane at 266 nm. The results shown are the cumulative effect of 72 μs exposure (12000 laser pulses).

to assign the ionization of the parent molecule to a $1+1$ resonantly enhanced multiphoton ionization process which proceeds through the B $(\pi\pi^*)$ resonant level [11,12]. The ions are formed within a solvent cage and proceed to react with surrounding species. In the case of hexyloxybenzene, it is the solvent reacting with the $C_6H_5O^+$ fragment ion, while for phenoxyphenol, the fragment ion must encounter a second, neutral phenol molecule. The results from the gas saturated liquid samples present additional data with regard to the nature of the reactions. Electron scavengers such as SF_6 and O_2 hinder geminate recombination and stimulate free ion production [4,13]. One would expect that the presence of the scavenger would increase the yield of ion–molecule products, *if free ions were necessary for reactions or if the reaction occurred through an excited state of phenol produced by recombination of the geminate pair*. Instead, the data in table 1 indicate that whether saturated with O_2 or SF_6, the quantum yields are not significantly different. The implication is that ion chemistry may compete with geminate pair recombination, rather than result from reactions with free ions, i.e. the ion–molecule chemistry may, at least in the case of the hexyloxybenzene formation, occur before the geminate pairs separate. This is consistent with the general time scale of geminate 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 [13]. However, the reaction to produce the phenoxyphenol must involve free ions, since the initially

created phenoxy cation will be surrounded by h... ane molecules. The fact that electron scavenger... not increase the yield of this product indicates t... the reaction rate is extremely fast. More informat... have been the experiments involving a positive... scavenger, decalin [14]. The presence of this... cies, in concentrations of 0.088 M, decreased... quantum yield of both products by a factor of... proximately two, indicating that the reactive pro... involved phenol-derived cations. Moreover, the i... ization potential of decalin is 9.6 eV [15], more t... 1 eV greater than that of phenol. One would no... pect, on purely energetic grounds, to observe sim... charge transfer from phenol to decalin. Howeve... is energetically possible for a decalin molecule t... as a hydrogen atom donor to the phenoxy catio... regenerate the phenol cation and inhibit the... served chemistry. This process has been observe... other systems [16]. The observation of the s... enging behavior of decalin is a further indicatio... the presence of the phenoxy cation and, henc... three-photon excitation. Table 1 contains the va... of the quantum yield and $G(100\ eV)$ for all o... scavenger experiments. Note that the G value... flux dependent.

Fig. 2 presents the phenol concentration de... dence of the product formation rates. The ra... phenoxyphenol formation is shown to depend q... ratically on the phenol concentration, while h... oxybenzene concentration shows a linear de... dence upon this quantity. This is exactly the exp... dependence of these rates based upon a pseudo-... order (in the phenoxy cation concentration)... tion. Note that the phenol ion is the initially... duced species *and* the reactant, so that the squar... dependence of the positive ion scavenger [17... ically observed in geminate pair studies is no... plicable to this system. Again, the data suppo... interpretation of the observed chemistry as resu... from an ion–molecule reaction.

An attempt was made to compare the ion cu... with product formation to directly correlate... chemistry with ion production. Time-depen... MPI-induced current measurements were condu... for the same solutions as were used in the che... measurements. Fig. 3 shows a typical trace, as... as the increase in ion production with increasing... intensity plotted as signal current/laser energ...

Table 1
Quantum yields and $G(100\ eV)$ for scavenging reactions

Conditions	Quantum yield (phenoxyphenol)	Quantum yield (hexyloxybenzene)
with decalin [a]	6.4×10^{-3} (0.14)	1.4×10^{-3} (0.030)
without decalin [a]	1.3×10^{-2} (0.27)	2.8×10^{-2} (0.060)
air saturated [b]	1.3×10^{-2} (0.28)	2.9×10^{-3} (0.060)
oxygen saturated [b]	1.5×10^{-2} (0.31)	2.2×10^{-3} (0.044)
SF_6 saturated [b]	1.3×10^{-2} (0.28)	3.0×10^{-3} (0.063)

[a] Laser energy of 0.8 mJ pulse^{-1} and pulse width of 2.5 ns.
[b] Laser energy of 0.7 mJ pulse^{-1} and pulse width of 2.5 ns. The values in parentheses are $G(100\ eV)$.
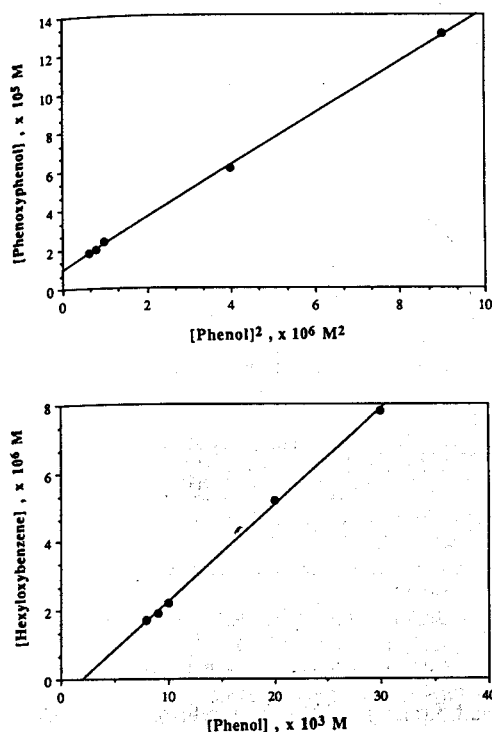
Fig. 2. Plot of product formation rates as a function of [phenol] or [phenol]^2 for 0.5 mJ incident laser energy. The solid line is the least-squares fit to the data.

Fig. 3. (a) Time dependence of the multiphoton ionization for a 10^{-3} M solution of phenol in n-hexane. The trace shown represents the average over 128 laser pulses at an applied field of 15 kV/cm and a pulse energy of 0.5 mJ. (b) The laser pulse energy dependence of the signal intensity. The slope of the least-squares fit shown in the figure is 1.9.

sus laser energy. The plot is linear indicating that the initial ion yield is second order in the number of photons present. This is further evidence of the ion–molecule nature of the reaction under study. The actual ion yield is somewhat lower than might initially be expected. The time-integrated number of ions at 0.5 mJ is $\approx 10^{13}$ or $\approx 2\%$ of the total photon flux. This quantity is, however, consistent with the fact that ion–molecule chemistry is occurring and that the ions do not simply drift, undisturbed, to the electrodes.

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
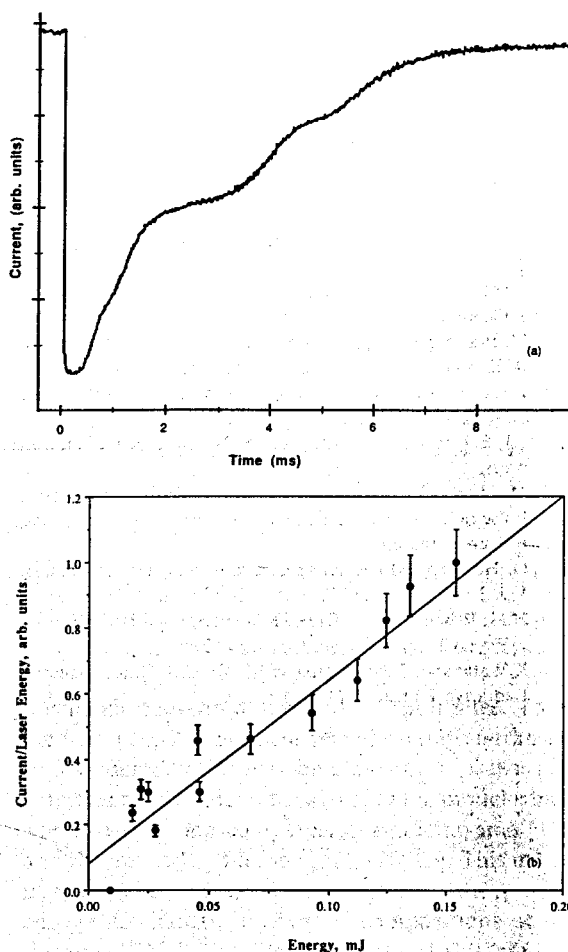
ion–molecule chemistry [4]. The method may also have synthetic applications and lead to the synthesis of new products through novel ion, rather than neutral photochemistry. Evidence of such reactivity has already been reported in the gas phase [18].

Acknowledgement

References

[1] R.P. Giugliano and J.J. BelBruno, J. Photochem. 37 (1987) 263;
T.M. Orlando, S.L. Anderson, J.R. Appling and M.G. White, J. Chem. Phys. 87 (1987) 852.

[2] M. Braun, J.Y. Fan, W. Fuss, K.L. Kompa, G. Mueller and W.E. Schmid, in: Methods of laser spectroscopy, eds. Y. Prior, A. Ben-Reuven and M. Rosenblun (Plenum Press, New York, 1987) pp. 367–378.

[3] J.J. BelBruno, G. Siuzdak and S. North, Laser Chem., in press.

[4] M. Ebert, J.P. Keene, A.J. Swallow and P. Wardman, eds., Pulse radioloysis (Academic Press, New York, 1965), and references therein.

[5] G. Herzberg, Molecular spectra and molecular structures, Vol. 3 (Van Nostrand Reinhold, New York, 1966).

[6] H.M. Rosenstock, K. Draxl, B.W. Steiner and J.T. Henon, J. Phys. Chem. Ref. Data 6 (1977) 1296;
K.Watanabe, T. Nakayama and J. Mottl, J. Quant. Spectry. Radiative Transfer 2 (1962) 369.

[7] H. Faidas and K. Siomos, J. Chem. Phys. 87 (1987) 509;
T.W. Scott and A.C. Albrecht J. Chem. Phys. 74 (1981) 3807.

[8] L.I. Grossweiner and W.A. Mulac, Radiat. Res. 10 (1959) 515.

[9] J.J. Yang, M.A. El-Sayed and F. Rebentrost, Chem. Phys. 96 (1985) 1.

[10] U. Lachish, A. Shafferman and G. Stein, J. Chem. Phys. (1976) 4205.

[11] R.M. Silverstein, G.C. Bassler and T.C. Morrill, Spectrometric identification of organic compounds (Wiley, New York, 1974).

[12] W.W. Simons, Sadtler handbook of ultraviolet spectra (Sadtler, Philadelphia, 1979).

[13] S.G. Lias and P. Ausloos, Ion–molecule reactions: their role in radiation chemistry (Am. Chem. Soc., Washington, 197) ch. 2.

[14] M.C. Sauer, A.D. Trifunac, D.B. McDonald and R. Cooper, J. Phys. Chem. 88 (1984) 4096.

[15] P. Natalis, Bull. Roy. Soc. Liege 31 (1962) 803.

[16] D.W. Werst and A.D. Trifunac, Chem. Phys. Letters 1 (1986) 475.

[17] S. Rzad, R.H. Schuler and A. Hummel, J. Chem. Phys. (1969) 1369.

[18] J.J. BelBruno, P.B. Kobsa, R.T. Carl and R.P. Hughes, Phys. Chem. 91 (1987) 6198;
J.J. BelBruno, S.R. Greenfield, R.T. Carl and R.P. Hughes, J. Phys. Chem. 92 (1988) 2480.