

UV-Laser Induced Photo-Oxidation of Aqueous Benzene Solutions: Formation of Phenol

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Abstract. Aqueous solutions of benzene were irradiated by focussed KrF laser light. The formation of phenol together with varying amounts of 1,3-cyclopentadiene-1-carboxaldehyde was shown by uv absorption measurements. A mechanism for this photo-oxidation via benzene radical cations produced by 2-photon ionization of benzene is proposed. Comparative gas phase laser experiments and experiments with unfocussed laser beams were consistent with previous results using incoherent light sources.


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There is a growing body of literature on uv laser-induced multistep photoionization of organic molecules [1], benzene being one of the most studied examples. Since such experiments are commonly conducted in the gas phase, it appears interesting to investigate the extension of these concepts to liquid solutions. We thus attempted to generate benzene radical cations ($C_6H_6^+$) by multiphoton absorption in benzene assuming also that this species in the liquid might undergo less secondary fragmentation than in the gas. The cat-ions are expected to react rapidly with anions from the solvent, or from additional solutes, respectively, to form neutral products. Besides, the solvated electrons generated concomitantly might give rise to interesting chemical processes, too. The competing backreaction of the solvated electrons with the radical ions is expected to proceed sufficiently slowly that it would not dominate the process.


The photochemical literature on benzene is very extensive. Without attempting any completeness the results relevant to this study may roughly be summarized with reference to Fig. 1. The wavelengths of interest here are 249 nm (KrF laser) and 193 nm (ArF laser). The KrF laser excites the molecule in the first step on the vibrationally induced weak ($\epsilon \approx 251 \text{ mole}^{-1} \text{ cm}^{-1}$) transition ${}^1B_{2u} \leftarrow {}^1A_{1g}$ [2]. Two more intense absorption bands are found [2] at 205 nm ($\epsilon \approx 9000 \text{ l mole}^{-1} \text{ cm}^{-1}$) and at 190 nm

($\epsilon \approx 70,000 \text{ l mole}^{-1} \text{ cm}^{-1}$) which are assigned as ${}^1E_{1u} \leftarrow {}^1A_{1g}$ and ${}^1B_{1u} ({}^1E_{2g}) \leftarrow A_{1g}$. At both wavelengths a second uv laser photon will take the molecule into the ionization continuum (Fig. 1).

Irradiation of benzene with the Hg line at 253.7 nm gives benzvalene as the primary product [3] which upon hydrolysis forms 1,3-cyclopentadiene-1-carboxal-

dehyde -CHO [4–7]. This compound exhibits

an absorption maximum at 294 or 308 nm for pH 6 or 10, respectively [4]. Treatment of the aqueous solution with $NaBH_4$ causes this absorption to disappear and gives an unsaturated alcohol which absorbs at about 248 nm [5]. Quantum yields between $\Phi = 0.07$ [4] and $\Phi = 0.18$ [7] have been reported. Photolysis in

acidic media leads to the alcohol -OH [8–12].

A suggestion that the benzenium ion $C_6H_7^+$ may be the key intermediate here [8] has been rejected and benzvalene is generally accepted as the primary product [12].

Literature results concerning the gas phase photochemistry of benzene are somewhat inconsistent. Excitation at 253.7 nm and subsequent bubbling of the gas through water gave phenol as well as mucon-dialdehyde whereas the use of liquid benzene instead of water yielded biphenyl [13]. However, this product is reported also for the extensive irradiation of benzene vapor [14]. At 185 nm polymers [15–19] are strongly formed together with fulvene [17–19], *cis*- and *trans*-

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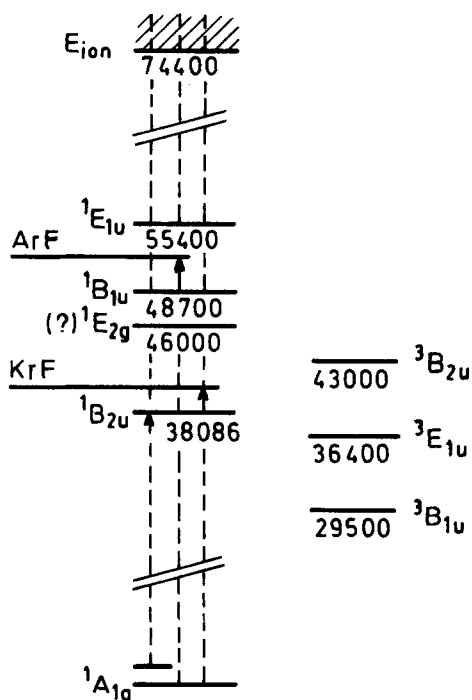
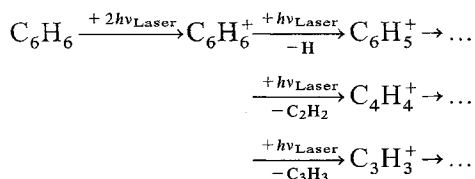


Fig. 1. Energy level scheme of benzene and transitions initiated by ArF and KrF laser radiation

1,3-hexadiene-5-ine [18, 19] and minor amounts of acetylene [16]. Dissociation into phenyl radicals at this wavelength was shown to be negligible [20].

As to the laser experiments the following results need to be mentioned here. When C_6H_6 vapor (20–50 Torr) is exposed to the unfocussed KrF laser [21] transient absorptions originating from $C_6H_6(^1B_{2u})$ are observed. With some delay after the laser pulse benzene clusters were identified but the formation of final photochemical products has not been investigated.

At very low pressures and high-power excimer laser irradiation in the vapor phase, ionization of benzene (as well as of many other molecules) is the dominant effect [22 and references therein]. Depending on the laser parameters excessive photofragmentation of the primary benzene ion may occur [23]:



Among the neutral species formed C_2 has been identified as a major product [24, 25]. The ion yields under some conditions can be very high although quantum yield measurements have not been done. No condensed phase uv-laser experiment of this particular molecule has been reported, although interesting data were described for the molecular ionization of surface

species (see, for example: amino-acids [26]) and ionic compounds in liquid solutions [27]. It is then fair to say that multiphoton ionization has so far not yet been used as a photochemical concept.

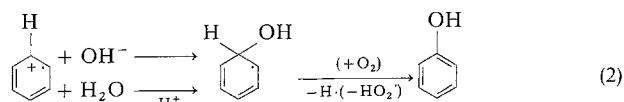
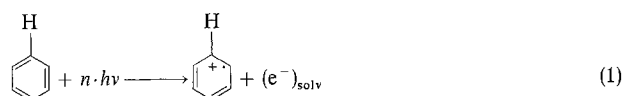
1. Results and Discussion

The laser used here was a standard excimer laser (Lambda Physik EMG 102). In the first set of experiments up to 100 pulses of 40 mJ (pulse duration ca. 20 ns) at 249 nm were applied to saturated aqueous benzene solutions contained in cuvettes of $10 \times 10 \times 50 \text{ mm}^3$. The laser beam cross section was circular with 8 mm diameter (unfocussed) and the focal spot ($f = 20 \text{ cm}$ lens) was $0.5 \times 1 \text{ mm}^2$ corresponding to a power density of ca. 10^8 W/cm^2 . No precaution was taken to eliminate oxygen from the solutions. UV absorption spectroscopy was done with a BECKMAN UV-5270 instrument.

Both focussed and unfocussed KrF laser beams were used. Unfocussed light led only to the formation of the known product 1,3-cyclopentadiene-1-carboxaldehyde. This was manifested by the characteristic uv absorptions at 294 nm (pH=6) and 308 nm (pH=10) which disappeared upon addition of $NaBH_4$ to the solution. If focussed KrF radiation was used instead, new absorption bands at 269 and 275 nm appeared. In addition, a small absorption maximum at 292 nm was found indicating the presence of minor amounts of the aldehyde. Treatment with $NaBH_4$ reduced this absorption and revealed the existence of another small shoulder at 285 nm. The absorptions at 269 and 275 nm first grew with continuing irradiation, then seemed to reach a photostationary state after about 100 pulses and finally could be seen to decrease if the irradiation was carried on. At the end of the pulse sequence also a continuous absorption was superimposed on the band structure. Each laser pulse produced a reddish fluorescence and some gas evolution.

The product absorption described can be understood on the assumption that phenol is formed. The uv-spectra measured were identical to those of reference phenol/water mixtures. A quantum-yield has not been determined exactly, but it is estimated to be $\leq 10^{-3}$.

We thus propose the following mechanism.



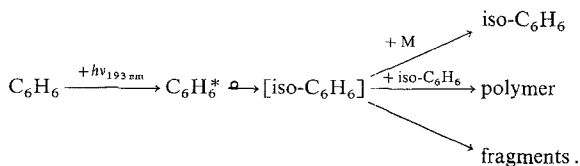
It may be assumed that substituents other than OH^- can be introduced in the same way and that the same scheme can be applied to other molecular substrates. We are aware of the fact that similar results are produced by radiation-chemical experiments [28–31], and that by irradiation of aqueous benzene solutions with γ -rays, x-rays, or high energy electrons phenol is formed, too. The mechanism there, however, is greatly different. Whereas in the laser case one is specifically exciting the minor component of the benzene/water system in one of its absorption bands, by the irradiation with high energy particles the major part, water is decomposed. The intermediates (e^-)_{solv}, $\text{H}\cdot$, $\text{OH}\cdot$, $\text{HO}_2\cdot$ then react with benzene to give phenol and mucondialdehyde by a radical pathway. Although it has been shown recently that high power uv laser pulses may also decompose H_2O in the same way [32], this possibility must be disregarded in the present case.

The back-reaction of the primary step (1) must be assumed to be relatively fast. In addition, deprotonation may occur on a ns time scale for certain molecules.



Thus, Bryant et al. [33] proposed as a model that the ionization process leads to a complex between the radical (ion) and the solvated electron, where up to $1\ \mu\text{s}$ dissociation competes with recombination. Our experimental results do not permit any detailed statements about these effects in the case of benzene. However, such a competition to the probably very fast addition of the radical cations to OH^- anions might explain the rather low quantum yield.

Supplementary measurements aimed at an investigation of the laser photochemistry of benzene in the $^1B_{1u}$ or $^1E_{1u}$ state. These states can be populated supposedly by ArF laser radiation at 193 nm. To this end 90 Torr benzene vapor were exposed to the output of this laser. Figure 2 reproduces the results showing that C_2H_2 and C_4H_2 are the only volatile products. These findings may be explained with reference to [15] by the following scheme:



Iso- C_6H_6 could be considered to be an isomer of benzene (e.g. fulvene, hexadienine), but may also be highly

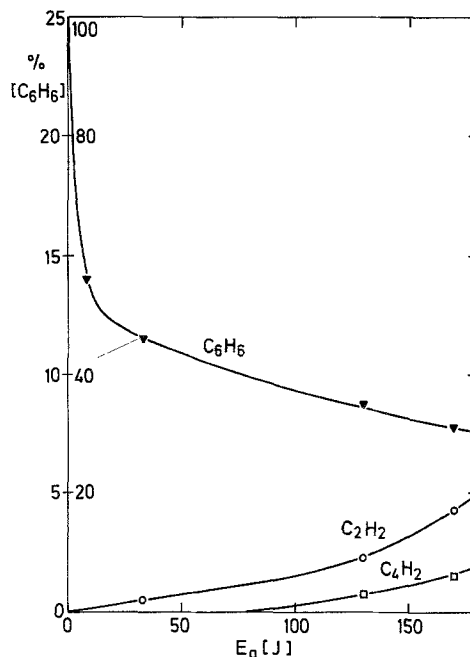


Fig. 2. ArF-laser photolysis of C_6H_6 (90.0 Torr). Increase of products (left-hand scale) and decrease of benzene (right-hand scale), based upon the initial C_6H_6 pressure, as a function of the energy absorbed

vibrationally excited benzene in the electronic groundstate after internal conversion. It is conceivable that C_4H_2 might be a secondary product resulting from the photolysis of C_2H_2 .

In conclusion this letter provides evidence for the formation of phenol from benzene via multiphoton ionization. This might open up new possibilities for excimer laser photochemistry. Further work is intended to evaluate the validity and the limits of this new scheme.

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