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Laser Flash Photolysis of Benzene. IV. Physicochemical Properties of Mist Produced by Laser Excitation†

Nobuaki Nakashima and Keitaro Yoshihara*
Institute for Molecular Science, Myodaiji, Okazaki 444

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Mist formation is observed when gaseous benzene (8—75 Torr) (1 Torr=133.322 Pa) with oxygen ($\lesssim 10^{-5}$—860 Torr) is irradiated by a KrF excimer laser. By measuring the falling speed, the size of droplets in the mist is determined to be 2 to 6 μm depending on gas pressure. The number of droplets produced by irradiation with a 100 mJ/cm^2 pulse is estimated to be 1×10^5/cm^3 by measuring the benzene pressure change and by turbidity measurement. The disappearance yield of benzene is 0.1 and phenol is identified with a quantum yield of 0.01. The nucleus is produced by two-photon excitation of benzene and allowed to grow into mist through a subsequent oxidation and/or polymerization reaction.

During the course of a laser-flash photolytic study of gaseous benzene,[1,2] we observed that laser beam will often cause mist to appear. The mist causes intense Mie scattering of monitor laser light and is easily visible in the form of falling "mist" or "rain." This laser-induced mist or particle formation seems to be the first observation with organic systems.

In this paper we report some physical and chemical properties of the mist studied with light scattering and transient absorption. The size of droplets in the mist was determined by measuring the falling speed. The number of droplets was estimated by observing the benzene pressure change and also by turbidity measurement. A possible mechanism for the photochemical formation of nucleus and for the enhancement of mist formation with oxygen is discussed.

Laser-induced solid particle formation has recently been observed in several other systems with simple molecules and/or metal vapors. Formation of solid alkali hydrides from alkali metal vapor and H_2 (Refs. 3 and 4) is induced by irradiation with a CW laser. Produced particles are called "laser snow," because they are white solid and fall down by gravity. Evolution of particles from NO_2 and SO_2 (Ref. 5) and of sulfur or aerosols from SF_6+H_2, CS_2, and Cl_2CS (Refs. 6,7, and 8) are also recognized.

Experimental

Gaseous benzene was excited by a KrF excimer laser (Lambda Physik EMG 500), at 248 nm, with typical output energy of 100 mJ and a pulse halfwidth of 15 ns. The laser beam with an area of 2.5×0.5 cm^2 was not focused for most experiments unless otherwise indicated. Transient absorption[2] and light scattering were measured in the perpendicular direction with a pulsed Xe lamp (EG & G 265UV) and a He–Ne laser, respectively. The intensity of light from a He–Ne laser scattered by mist was monitored with a photomultiplier at right angles through an $f=1.5$ lens and recorded on an X-T recorder.

A monitoring light at 260 nm was obtained from a D_2 lamp through a Shimadzu-Bausch & Lomb monochromator and was used for determining the concentration (pressure) of benzene. The output signal, run through a Nikon P250 monochromator and two Ortec Brookdeal 9503 lock-in amplifiers, was further normalized with a ratio meter model 5043. The linearity of absorbance at 260 nm held up to 0.9 in absorbance units, corresponding to 100 Torr cm of gaseous benzene, when the smallest slit width ($\Delta\lambda\approx$ 0.15 nm) of the monochromator was used. Absorption spectra were measured on a Cary 17 spectrophotometer.

A conventional greaseless vacuum line was used for sample preparation with a Baratron pressure gauge 310BHS-1000. Back pressure was 1×10^{-5} Torr. A quartz cell was closed with a J. Young greaseless stopcock. Our "oxygen free" sample was prepared by complete degassing with freeze-pump-thaw cycles and closed off by fusing the tubing. Quartz cells were baked at about 490 °C for several hours before use. Usually the sample was excited at intervals of 15 min and was renewed after 5 laser shots.

Benzene (J. T. Baker, stated purity of 99.98%), oxygen (99.98%), nitrogen (99.9995%), SF_6 (99.9%), and *cis*-2-butene (99%) were used without further purification. All the gases were produced by Nippon Sanso.

Results

Observation of Mist Formation. In the flash photolysis experiment with a KrF excimer laser we visually observed mist formation when the sample was viewed under room light. Scattering from a He–Ne laser makes the presence of mist much clearer as shown in Fig. 1. Figure 2 shows the intensity of 90° light scattering by mist produced from a sample with 20 Torr of benzene and 0.08 Torr of oxygen. The mist formation is enhanced by oxygen; it is observable even in an "oxygen free" condition with the same pressure of benzene.

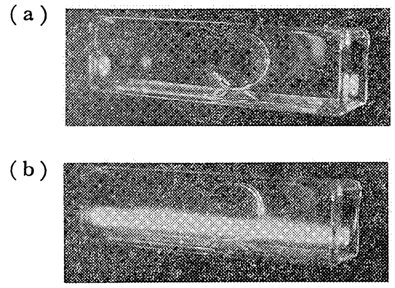

Fig. 1. Mie scattering by mist produced from gaseous benzene excited by a KrF laser.
a): Sample cell before irradiation, b): after irradiation of 40 Torr of benzene and 2 Torr of oxygen. The size of the sample cell is $4.0\times1.0\times1.0$ cm^3. The area of the laser beam is 2.5×0.5 cm^2. The sample is irradiated without focusing the beam.

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† Part III of this series is Ref. 2.

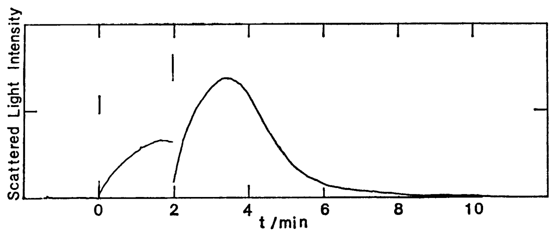


Fig. 2. Time course of the light scattered at 90° with 20 Torr of benzene and 0.08 Torr of oxygen.
The spikes indicate noise due to laser pulses. The light scatterings are quenched very quickly by subsequent laser excitations and then regenerated slowly.

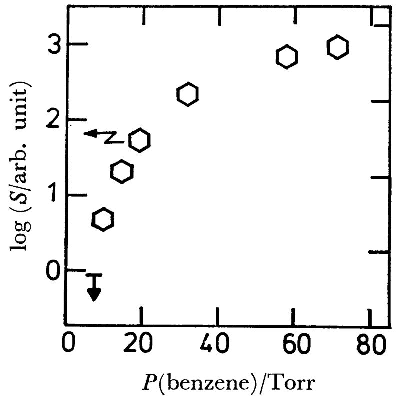


Fig. 3. Dependence of pressure of benzene on the scattered light intensity.
Peak height of the scattered light is plotted by ⬡; each sample contains 2 Torr of oxygen. A bar with an arrow at 7.5 Torr shows that the scattered signal was lower than the detection limit (the bar).

It takes the signal about 50 s to reach its peak and about the same time to decay. The rise time of the scattered light intensity is related to the rate of the nucleation process. Decay times simply depend on the falling speed of droplets, as discussed in the next section.

The scattered light intensity is decreased immediately by subsequent laser shots as shown in Fig. 2. This indicates that the mist absorbs the subsequent laser pulse and is destroyed easily. It is suggested that component molecules of the mist are relatively small and bound together by a small molecular interaction.

The scattered light intensity is increased more than 300 times upon increasing the pressure of benzene from 8 to 75 Torr. Figure 3 shows scattered light intensity *vs.* pressure of benzene in the presence of 2 Torr of oxygen. We do not observe any signal if the benzene pressure is less than 7.5 Torr. The concentration of nuclei is suggested to be too low to start nucleation at pressures less than 7.5 Torr.

The size of droplets has been determined to be 2—6 μm by measurement of the falling speed. The size can be evaluated using the equations[9)]

$$mg = 6\pi\eta rv, \quad m = \frac{4}{3}\pi r^3\rho, \tag{1}$$

where η is viscosity of mixed gas, r is radius of droplet, v is falling speed, ρ is density of droplet, and g is gravity. For the system consisting of 21 Torr of benzene, 2.1 Torr of oxygen, and 207 Torr of nitrogen, η is evaluated to be 1.57×10^{-4} P (1 P=0.1 Pa s). We do not know all of the compositions of the droplets, so that ρ cannot be given any accurate value. However, we presume $\rho=1.0$ g/cm^3. This seems to be a feasible approximation since the starting materials for the droplets are benzene and oxygen and densities of most organic hydrocarbons are close to unity. For example, the density of benzene is 0.88 g/cm^3 and that of phenol (one of photoproducts) 1.07 g/cm^3. If we measure v, the size will be given by Eq. 1.

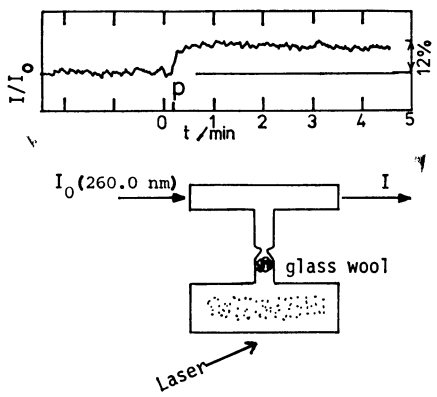


Fig. 4. Junction cell experiment. The larger cell was irradiated with 20 laser shots at 2 Hz.
Irradiation started at 0 min and stopped at p in the figure. Pressure change was monitored at 260 nm ($6_0^1 16_1^1$ transition). The actual change in transmittance was 3%, which corresponds to a quantum yield of 0.12 after correcting the volume of irradiation and the laser energy. The sample cell contains 23.2 Torr of benzene and 2.3 Torr of oxygen.

The mist produced by irradiation begins to fall. The speed is so low as to be measured visually. The position of the fastest droplet is plotted as a function of time. For the above case v was $(1.8\pm0.5)\times10^{-2}$ cm/s. Then, the diameter ($2r$) of the droplets is $(2.3\pm0.3)\times10^{-4}$ cm. The size of 2—6 μm is obtained in the benzene pressure range 8—75 Torr. An increase in the size accompanies an increase in the pressure of benzene.

By knowing the approximate size of droplets, we can determine an approximate number of the droplets produced, in two independent ways: one uses pressure change of gaseous benzene due to mist formation and the other is based on turbidity measurement of mist. Decrease in benzene pressure can be determined by change in absorbance at 260 nm, which corresponds to the $6_0^1 16_1^1$ transition. As shown in Fig. 4, two quartz cells are connected by a thin neck, one being the sample cell for excitation of benzene and the other being the monitoring cell.

The yield for the decrease in benzene pressure is 0.13 ± 0.02 with and without oxygen. Taking into account the size of droplet (2.5 μm), the number of droplets is obtained to be 1.3×10^5 /cm^3 at a laser excitation of 125 mJ/cm^2. Experimental details are as follows: A mixture of benzene (23.2 Torr) and oxygen (2.3 Torr) is irradiated by 20 pulses of a 156

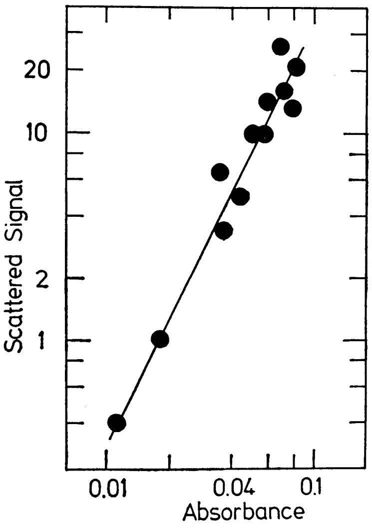


Fig. 5. Scattered light intensity *vs.* absorbance of the excited singlet state observed at 256 nm.
Pressure of benzene is 20 Torr with 0.08 Torr of oxygen. The straight line shows a slope of 2.0.

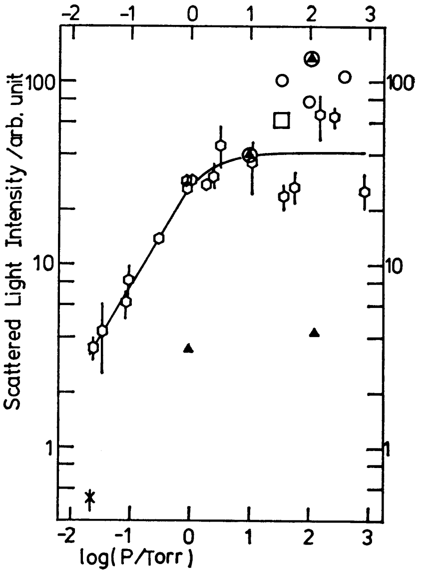


Fig. 6. Dependence of foreign gases on the scattered light intensity.
The benzene pressure for all experiments is 20 Torr. ○: Pressure of oxygen is denoted on the abscissa, □, ⊛, ○: effects of *cis*-2-butene, SF_6, and nitrogen, respectively are given. In these cases 2 Torr of oxygen is included and the total pressures of foreign gases are denoted on the abscissa. x: 20 Torr of benzene with an oxygen pressure less than 10^{-5} Torr, ▲: benzene and SF_6 with oxygen pressure also less than 10^{-5} Torr.

mJ laser with a cross section of 1.25 cm^2 at 2 Hz. About 2×10^{18} photons are absorbed in a total volume of 5 cm^3. In order to estimate the number of droplets, it is necessary to assume the volume of component molecules. The approximate volume of phenol (0.53 nm^3 is used here as that of the component molecules. Glass wool was inserted at the neck of the quartz cell in order to prevent photoproducts from flowing into the monitoring cell. If the glass wool was not added, photoproducts canceled out the change in absorbance due to mist formation.

During the sample irradiation at 2 Hz, the signal shows no change. Just after stopping the irradiation (denoted as p in Fig. 4), the pressure of benzene begin to decrease, reaching the minimum value within 10 s. This observation indicates that the mist is destroyed by the subsequent laser shots as seen in Fig. 2. The slow increase after a few minutes indicates a flowing-in of photoproducts.

Turbidity was measured in order to estimate the number of droplets. Extinction change due to scattering by droplets is expressed as

$$\tau = \frac{1}{a}\ln\frac{I_0}{I} = \pi r^2 K N, \tag{2}$$

where a is the path length of the monitoring cell (2.5 cm), r is the radius of the droplet (1.25 μm), and K is the average total Mie scattering cross section (2.0 used here). In the case of 45 Torr benzene with 2 Torr of oxygen, τ was 1×10^{-2} /cm for the first laser shot of 100 mJ/cm^2 and then the number (N) is given as 1×10^5 /cm^3, which is in agreement with that obtained by the pressure change of benzene in the previous section. The value K=2.0 is a good approximation, considering the size parameter of Mie scattering.[10)]

Power Dependence, Effect of Foreign Gases, and Photoproducts. Figure 5 shows scattered light intensity *vs.* absorbance of the excited state of benzene. The scattered light intensity clearly gives a quadratic dependence on the S_1 concentration. The latter quantity was obtained by observing the intensity of the $S_n \leftarrow S_1$ absorption at 256 nm.[1,2)] The absorbance of 0.1 corresponds to *ca.* 0.4 Torr of the S_1 concentration.

We could not observe any scattered signal when a Xe lamp was used as an exciting light source instead of the laser. These results indicates clearly that multiphoton excitation makes the mist formation possible, but that one-photon excitation does not. The energy of the Xe lamp was 1.3 mJ in the range of 220—250 nm at the sample cell. In order to avoid exciting benzene into the S_3 state and heating it up by IR light, methanol in a 2 cm cell was used as a filter.[11)] A sample with 42 Torr of benzene and 8 Torr of oxygen was excited at 0.7 Hz and a total energy of 200 mJ was dumped in.

Pressure effect of foreign gases on scattered light intensity makes the role of oxygen clear. An oxygen-free sample shows a very weak signal as shown in Fig. 6 (denoted by ×). An increase in oxygen pressure (denoted by ○) is accompanied by an enhancement of scattered light intensity in the range from 2×10^{-2} to 2 Torr. This observation indicates that oxidation reaction is the major reaction which causes the mist formation.

cis-2-Butene, SF_6, or nitrogen does not seem to have any significant effect on the intensity when added to a system of 20 Torr of benzene and 2 Torr of oxygen. It is worth noting that only SF_6 makes aerosol. This may occur according to a mechanism similar to that for other sulfur-containing compounds.[6—8)] This is the

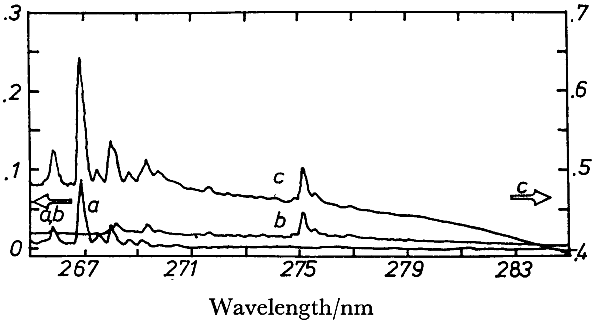


Fig. 7. Absorption spectra of 48 Torr of benzene with 5 Torr of oxygen after irradiation with 15 shots of 150 mJ laser energy.
a: Benzene (reference spectrum), b: reference absorption spectrum of phenol with a pressure of 0.35 Torr, and c: after laser irradiation.

reason that the oxygen free sample with SF_6 shows a larger signal than the ones without SF_6.

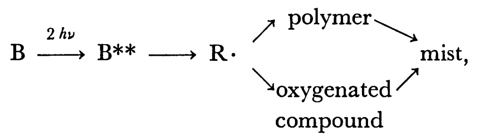
The consumption yield of benzene upon excitation was 0.08±0.02 with and without oxygen after several hours. In order to avoid photolysing mist, the sample was irradiated only every 4 min so that most of the droplets fell down to the bottom of the cell before the subsequent laser shot came. The comsumption yield of 0.08 roughly coincides with the yield of pressure change of 0.13 obtained in the previous section. This reasonable agreement suggests that the major part of the pressure change due to mist formation can be ascribed to the nucleation of permanent photoproducts of benzene and not to aggregation of pure benzene.

Phenol was observed with a quantum yield of 0.01 as shown in Fig. 7. In addition to phenol, we obtained volatile species with absorption spectra shorter than 230 nm and nonvolatile species with a shoulder around 290 nm. The latter was observed only in the sample with oxygen. Phenol has been reported as a major photo-oxidation product in the gas phase,[12,13] though there is no report on the quantum yield of phenol formation. The shoulder around 290 nm might be for mucondialdehyde, which has been detected as a photo-oxidation product in the gas phase[13] as well as in pure liquid benzene.[14] A larger yield of polymer formation was observed in the sample without oxygen.

Discussion

Two-photon Absorption and Primary Photoproducts. There are a few possible processes for the two-photon mechanism leading to the formation of nuclei: 1) simultaneous two-photon absorption; 2) two-step excitation by energy transfer between excited singlet and/or triplet molecules, 3) consecutive two-step absorption *via* excited state. The major process is suggested to result from effects of foreign gases. Oxygen quenches the lowest excited singlet state of benzene with a rate constant of $1.02\times10^{11}\ \mathrm{M}^{-1}\,\mathrm{s}^{-1}$ and the triplet state with $9.5\times10^{9}\ \mathrm{M}^{-1}\,\mathrm{s}^{-1}$ (the same order of magnitude as that of *cis*-2-butene) (Refs. 15 and 16). Then the lifetime in the presence of 860 Torr of oxygen is expected to be 0.12 ns for the singlet state and 1.2 ns for the triplet state. These lifetimes are too short for excited molecules to collide among themselves and not long enough to absorb the second photon consecutively. The scattered signal intensity does not decrease at higher pressures of oxygen. Therefore, two-step excitation by energy transfer between two excited molecules can be excluded. The consecutive two-step excitation mechanism *via* excited states may be included to a small extent. The major process is suggested to be the simultaneous two-photon absorption.

In any two-photon processes, benzene is excited in the VUV region of 8.6—10 eV. The photochemistry of benzene by continuous light sources in the VUV region suggests that precursors for the mist produced by two-photon absorption are likely to be radicals with linear structure. With Kr (116.5 nm) and Xe (147 nm) lines, polymer formation is the major process and acetylene is produced with a quantum yield of *ca.* 0.1. The photochemical consumption yield has been estimated to be almost 1.0 at lower pressures.[17,18] On the other hand, the photochemical consumption yield is 0.1 by laser excitation in our experiment. The cross section of the absorption at the laser wavelength is expected to be larger under higher power irradiation. Several percent of increase in the cross section was observed at 80 Torr of benzene when incident laser power is varied from 40 to 150 mJ/cm². Hexatriene is accumulated easily by irradiation of benzene in cyclohexane with a KrF laser,[19] and the yield of polymer is higher in the absence of oxygen. These observations also support that the major primary photoproducts are linear radicals. The major processes are suggested to be



$$\begin{tikzcd} & & & \text{polymer} \arrow[dr] & \\ \mathrm{B} \arrow[r, "2h\nu"] & \mathrm{B}^{**} \arrow[r] & \mathrm{R}\cdot \arrow[ur] \arrow[dr] & & \text{mist,} \\ & & & \begin{array}{c}\text{oxygenated}\\\text{compound}\end{array} \arrow[ur] & \end{tikzcd} \qquad (3)$$

where B^{**} is a higher excited state of benzene and R· is a linear radical. Other minor photoproducts are also conceivable, *i.e.*, cationic species (monomer or dimer cations) and phenyl radicals, which may be a primary source of phenol.

Effect of Oxygen on Mist Formation. Organic mist formation requires accumulation of condensable species in excess of their gas-phase saturation conditions. Linear radicals are known to react with one another as well as to react with benzene and produce various derivatives by photolysis in solution.[20] All of these photoproducts are expected to show vapor pressures lower by several orders of magnitude than those of six-carbon parent molecules. Thus they would form mist even in the absence of oxygen according to the upper process of Scheme 3.

Linear biradicals formed by ring cleavage will be very easily oxidized and will give many kinds of bifunctional oxygenated compounds. Rates of addition reaction of oxygen have been reported as a few percent of the collisional frequency for simple radicals and equilibrium constants are very large, of the order of $10^{10}\ \mathrm{Torr}^{-1}$ (Ref. 21). Oxidation makes volatility lower by more than several orders of magnitude; in particular, those of dicarboxylic acids are about 9 orders of magnitude lower than those of the parent molecules. The nucleation is much enhanced in the presence of oxygen according to the lower process of Scheme 3.

Formation of phenol was observed as shown in Fig. 7. In the course of formation of phenol, atomic oxygen (^3P) can be produced upon excitation of gaseous benzene.[12,22] It is well known that atomic oxygen reacts with benzene to produce phenol and also allows linear radicals to be oxidized.[23] These oxidation reactions contribute to the enhancement of mist formation.

The mechanism for the photochemical aerosol formation in urban atomosphere has been studied in detail.[24] Hydrocarbons are oxidized by ozone and/ or hydroxyl radicals to form aldehydes, alcohols, or carboxylic acids. These oxygenated compounds have a low volatility. Then, no polymerization is necessary to form aerosols from cyclic olefins, even when they are present at trace concentrations (below 10^{-6} Torr) in ambient air.[24] These processes are similar to what we observed with benzene.

We reported that the initial stage of light-induced condensation of benzene was found in nanosecond time-resolved difference spectra.[1] However, we have recently found that these spectra can also be explained in terms of temperature rise due to nonradiative transitions.[25] The observations presented in this report, *i.e.*, the effects of foreign gas and laser power on mist formation and the results from the junction cell experiment, do not support the tentative explanation given in the previous report.

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