EXCITATION DENSITY EFFECT ON THE DECOMPOSITION OF LIQUID BENZENE BY ArF EXCIMER LASER (193 nm) IRRADIATION

Ryuzi Katoh
National Institute of Materials and Chemical Research (NIMC),
Tsukuba, Ibaraki 305-8565, Japan.

When a high power laser irradiates a target material, excited molecules can be produced at high density. As a result, high temperature and high pressure conditions can result in various unexpected reactions which do not occur with conventional light sources, such as a mercury-lamp. In order to know the effect of the excitation density in detail, we studied decomposition of liquid benzene with an ArF excimer laser (λ = 193 nm) as a function of laser fluence.

At low laser fluence, the irradiated liquid was colorless, but at higher fluence it turned black, which is due to soots formation. We analyzed aromatic products, such as biphenyl, m-terphenyl and phenanthrene, with a HPLC as a function of laser fluence. For biphenyl, the yield seems constant in the low laser fluence range. Above 7 mJ / cm^2, the biphenyl yield increases steeply up tp 30 mJ / cm^2 and then, decreases. The sooty material appeares above 20 mJ / cm^2 and the yield increases steeply.

The production of biphenyl is due to the C-H bond dissociation of benzene and following phenyl radicals recombination. There are two possible mechanisms for the generation of phenyl radical through multi-photon process. One is the decomposition of a highly excited state populated through multi-photon excitation (MP process). The other is the pyrolysis of the ground state benzene by heat induced by non-radiative decay of excited molecules (PY process).

Multi-photon (MP) process

C_6H_6 → (Photons) $C_6H_6^{**}$ → (Decomposition of the highly excited molecule) C_6H_5 + H (1)

Pyrolysis (PY) process

C_6H_6 → (Photons) $C_6H_6^{**}$ → (Non-radiative decay) heat → (Decomposition of the ground state molecule) C_6H_5 + H (2)

In the case of the MP process, the yield of biphenyl is expected to be proportional to the number of the highly excited molecule, whereas, for the PY process, proportional to the density of the highly excited molecules. In order to change the density of highly excited molecules, we add cyclohexane which does not absorb for 193 nm photon. From the result of the decomposition of benzene / cyclohexane mixture, we conclude that the PY process is dominant. We can estimate the temperature rise ΔT in the irradiated volume. If the laser fluence is 100 mJ/cm^2, ΔT can be estimated to be 14000 K at 193 nm. This high temperature is plausible for the PY process.