



Title	Investigation of photodegradation mechanism in laser dyes by detection of triplet-molecules and free radicals induced by laser light
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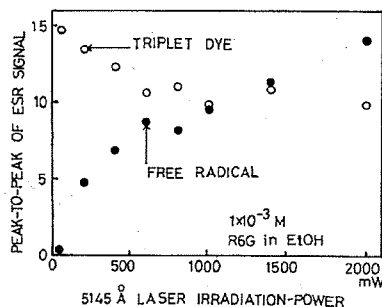


Fig. 2. 5145 Å laser-irradiation-power dependences of the peak-to-peak esr signals due to the triplet-dyes and of those due to the photoinduced free radicals after degradation.

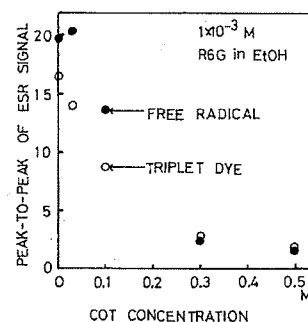


Fig. 3. COT concentration dependences of the peak-to-peak esr signals due to the triplet-dyes before degradation and of those due to the free radicals after UV irradiation.

1.5 Investigation of Photodegradation Mechanism in Laser Dyes by Detection of Triplet-Molecules and Free Radicals Induced by Laser Light, Mikio Yamashita and Hiroshi Kashiwagi, Electrotechnical Laboratory, Tokyo, Japan, and Hidenori Ikeda, Keio University, Yokohama, Japan

(15 min)

Photodegradation of organic dyes has severely limited the life of the laser, but the degradation mechanism is not yet well understood. The study on the degradation has been made so far by measuring changes in the absorption and fluorescent spectra of the dye solution before and after photodegradation. We are investigating the photodegradation mechanism by a quite different method where laser-induced free radicals and triplet-dyes are directly monitored at 77 K using an esr technique during and after

laser irradiation. In comparison with measuring optical spectra our method has the following merits; (1) the dye molecules in the first triplet excited state and the photochemically produced free radicals can be directly detected, and (2) this method is much more sensitive for the photochemical paramagnetic-products in the dye solution.

Each dye—R6G, RB, RS, AR, and FDS—from the Eastman Kodak and Tokyo Kasei Kogyo Cos., was dissolved in ethanol, methanol or DMSO at 1×10^{-3} M concentration. The oxygen-free solution was outgassed by a freeze-thaw process and sealed in a 4 mm-o.d. quartz tube. Both the esr spectra of the H_{\min} line corresponding to $\Delta m = \pm 2$ transitions in the triplet-dyes and of the free radicals induced by laser light were recorded with a Varian E-4 spectrometer with an optical transmission cavity. The glassy solution, cooled by inserting into liquid nitrogen in a quartz Dewar, was irradiated by an unfocused beam with the UV (3511 + 3638 Å) or 5145 Å wavelength of an Ar ion laser.

At first it was found that continuous excitation for several minutes by UV or 5145 Å beams produced the esr signals of the free radicals and decreased the intensity of the H_{\min} line which is proportional to the triplet-dye concentration. These phenomena appeared in the case of UV excitation under less excitation-power and -time than in the case of visible excitation, and the

shapes of the spectra due to the free radicals produced were different, as shown in Fig. 1. The peak-to-peak esr signals due to the free radicals produced after laser irradiation with 5145 Å for five minutes and those due to the triplet-dyes (which were recorded during irradiation of 5145 Å beam with very low power after the degradation) are given as a function of the continuous irradiation power in Fig. 2.

Furthermore, the investigation of the effects of different dyes (R6G, RB, RS, AR, and FDS) and solvents (ethanol, methanol, and DMSO) on the UV laser-produced radical-spectra has shown the spectrum shape depends on the solvent molecule but hardly depends on the molecular structure of the dye. The dependence of the peak-to-peak radical signals on the triplet molecular concentrations was examined for 1×10^{-3} M ethanolic R6G solutions with different COT concentrations after UV irradiation, as shown in Fig. 3. From these results, we consider that the chemical reaction between the triplet-dye molecules and the solvents dissolving the dye causes the photodegradation of the dye solution and produces the free radicals.

Fig. 1. Observed laser-induced derivative esr spectra of free radicals in 1×10^{-3} M ethanolic R6G solution at 77 K.

