Oxidation of Ethylamine to Glycine in Aqueous Solution induced by KrF Excimer Laser Irradiation

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KrF excimer laser irradiation of ethylamine in aqueous solution results in stepwise oxidation to give ethanolamine and glycine.

Hydroxyl and hydrogen radicals are strong oxidizing and reducing species, respectively. These radicals can be generated by homolytic dissociation of the H_2O molecule.[1] It is known that contact glow discharge electrolysis (CGDE),[2] plasma jet[3] and burning flame[4] are effective ways to produce these radicals in aqueous solution. Several organic reactions in aqueous solution were carried out by the use of such high-energy conditions.[2–4]

Letokhov and his coworkers[5] demonstrated that KrF excimer laser induces nonlinear photochemistry of aqueous solutions cleaving the O–H bond of water. In their experiment, water addition to maleic acid took place yielding a saturated hydroxy carboxylic acid (malic acid). The quantum yield of this product with a laser intensity (I) of 10^9 W cm^{-2} was reported to be higher than 1, which pointed to the production of free radicals in the course of the overall reaction. Liquid water as well as gaseous H_2O shows strong absorption around 10 eV (with a cross-section of 1.2×10^{-17} cm^2) which is associated with the $\sigma \rightarrow \sigma^*$ excitation in the vapour at 9.6 eV.[6] Subsequent to the first report by Donovan and coworkers,[7] Hodgson *et al.* also found that the two-photon excitation of H_2O at 248.5 nm (KrF; 1×10^9 W cm^{-2}) produces the C $^1B_1$ state which crosses with the B $^1A_1$ ($\sigma \rightarrow \sigma^*$) dissociative state producing a hot OH radical. This dissociative state is also correlated with the lowest excited state of H_2O at the dissociated limit with the H---OH configuration. Thus, the two-photon excitation at 248 nm of liquid water is reasonably expected to dissociate an H_2O molecule into H + OH fragments.

A KrF excimer laser (Lumonics TE-860, 120 mJ, 20 Hz) was used to irradiate a fused quartz cell containing an aqueous solution (30 ml) of ethylamine (1 mmol dm^{-3}) HCl (10 mmol dm^{-3}). The molar ratio of water to ethylamine is 5.6×10^4 and the contribution of the direct two-photon dissociation of ethylamine to the main reaction processes caused by H_2O dissociation is almost negligibly small under the acidic conditions. The use of a focusing lens with a focal length of 15 cm enabled us to perform high photon density excitation of water with the intensities of 5×10^8 to 2×10^9 W cm^{-2}. According to the result by Letokhov and his coworkers,[5] this power range is high enough to induce participation of water in reactions in aqueous solution. In order to follow the progress of the reactions, samples were removed every ten minutes, and analysed with a Hitachi 835 amino acid analyser. The variation in amounts of starting materials and products is shown in Fig. 1(*a*).

The amount of substrate decreased with the reaction time, and the oxidized products (ethanolamine **2**, aminoacetaldehyde **3** and glycine **4** increased to a maximum and then decreased. The maximum yields of ethanolamine **2**, amino-

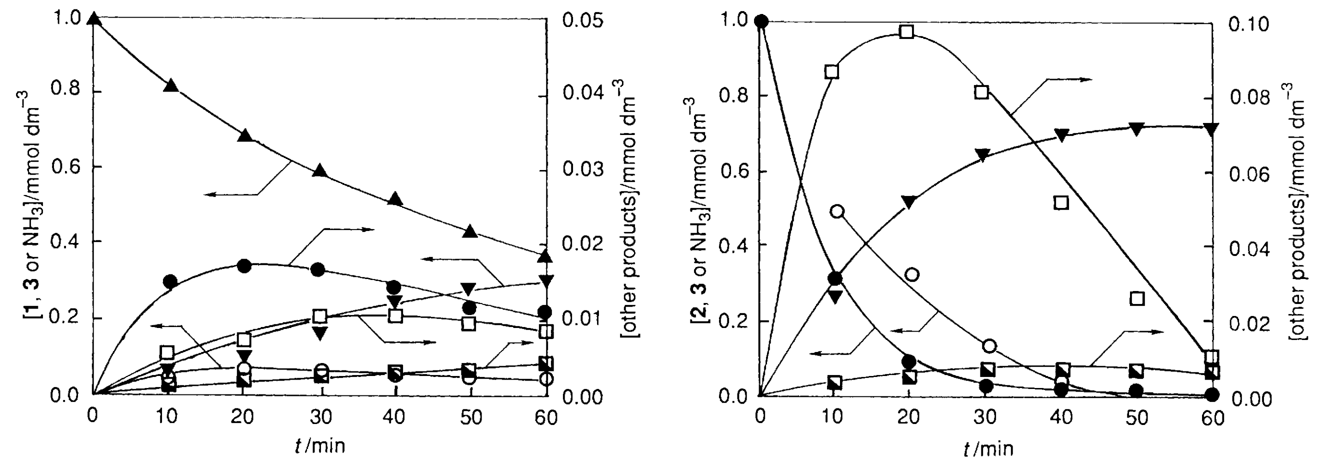
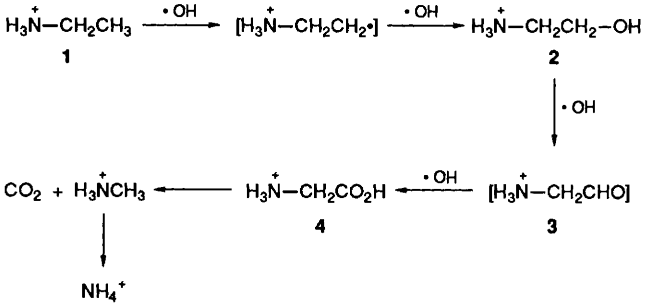


Fig. 1 Oxidation of (*a*) ethylamine (1.0 mmol l^{-1}) and (*b*) ethanolamine (1.0 mmol l^{-1}) in HCl (10 mmol l^{-1}) induced by KrF excimer laser irradiation: ▲: ethylamine; ●: ethanolamine; ▼: ammonia; □: glycine; ○: aminoacetaldehyde; ◧: methylamine



Scheme 1 Oxidation of ethylamine in HCl (10 mmol dm^{-3}) induced by KrF excimer laser irradiation

acetaldehyde **3** and glycine **4** were 1.7, 6.6 and 1.0% respectively. The yields of ethanolamine **2** and aminoacetaldehyde **3** reached maxima earlier than glycine **4** indicating that ethanolamine **2** is the primary product which is then oxidized through aminoacetaldehyde **3** to glycine **4**. Therefore, ethanolamine **2** was used as the starting material for further oxidation experiments. A solution of ethanolamine (1 mmol dm^{-3} in HCl (10 mmol dm^{-3}) was irradiated by a KrF excimer laser. The progress of the reaction is shown in Fig. 1(*b*). The maximum yield of glycine **4** was 10%. The low yield of glycine could be explained by its lability under the reaction conditions. For example, when glycine (1 mmol dm^{-3}) in HCl (10 mmol dm^{-3}) was irradiated by a KrF excimer laser, it decomposed rapidly to give ammonia.

The present results could be explained by the stepwise oxidation of the substrate (Scheme 1) by hydroxyl radicals in aqueous solution. To the best of our knowledge, this provides the first example of the oxidation of organic compounds in aqueous solution induced by KrF excimer laser irradiation.

The results indicate that the KrF excimer laser could be an interesting source for selective decomposition of water molecules to generate hydroxyl radicals in aqueous solution and a useful method to investigate the oxidation of organic compounds in aqueous solutions.

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