Mutagen Formation from Aromatic Compounds by Photochemical Reaction in Water Containing Nitrite Ion — Mutagen Formation from Naphthols and the Reaction Mechanism —
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We have been investigating photochemical mutagen formation from aromatic compounds in water containing nitrite or nitrate ion as a cause of mutagen formation in aquatic environments. In this report, we first summarize our earlier studies on photochemical mutagen formation from a wide variety of aromatic compounds in aqueous nitrite solution, and on the identification of p-nitrosophenol, 1-nitropyrene and hydroxynitrophenyls as the photoreaction products from phenol, pyrene and biphenyl, respectively, and then report on a subsequent study on the photoreaction of naphthols, showing that quinone production is also related to mutagen formation.

When naphthols were irradiated with UV light in aqueous nitrite solution under air, oxygen and nitrogen atmospheres, 2-naphthol gave a mutagenic product in an amount proportional to the irradiation time under air. The mutagen formation was greatly accelerated under oxygen, whereas irradiation under nitrogen gave no mutagen. 1-Naphthol gave scarcely any mutagen under any conditions.

The following seven compounds were isolated from the photoreaction products of 2-naphthol in aqueous nitrite solution under air: 1-nitro-2-naphthol, 1-nitroso-2-naphthol, isocoumarin, 5- or 8-nitro-2-naphthol, a mono-quinonoid dimer of 2-naphthol (NP-NQ), a dinitro-2-naphthol and 1,2-naphthoquinone. Among these compounds, 1-nitro-2-naphthol, 5- or 8-nitro-2-naphthol and a dinitro-2-naphthol exhibited a weak mutagenicity towards S. typhimurium TA98 without S9 mix. Although no major mutagen was isolated, it was found that irradiation of the solution of nonmutagenic NP-NQ with nitrite and of the mixed solution of 1,2-naphthoquinone and 1-nitro-2-naphthol without nitrite resulted in the formation of further mutagenic compounds. These results indicate that not only nitration but also quinone production is closely related to photochemical mutagen formation.

1-Naphthol was also found to give 2-nitro-1-naphthol, 2-nitroso-1-naphthol, 1,4-naphthoquinone and isocoumarin by photoreaction in aqueous nitrite solution under air. Therefore, the photoreactions of naphthols with and without nitrite under the three conditions were analyzed by HPLC in terms of degradation of naphthols and production of nitrosanaphthols, nitronaphthols, quinones and isocoumarin. It was proved that the reactions of nitration and naphthoquinone production both require oxygen. Consequently, the oxygen requirement for mutagen formation was attributable to those for nitration and quinone production from 2-naphthol. Nitronaphthols were presumed to be produced directly by the reaction of photo-induced naphthoxy radical with NO₃ radical formed by oxidation of photo-induced NO radical. Both 1,2- and 1,4-naphthoquinones were found to be converted photochemically to photo-stable isocoumarin, which exhibited only ambiguous mutagenicity, at different rates. 1-Naphthol, compared with 2-naphthol, was hardly nitrated and was easily converted to isocoumarin, and such reactivity was presumed to be the main reason for the lack of mutagen formation.