

Study on the Production of Toxic Nitro derivatives from Aromatic Compounds

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DESCRIPTION

Photochemical reactions play a significant role in the processes in sunny natural surface waters. They are essential in the transformation of various naturally occurring chemicals and bio recalcitrant pollutants, and frequently lead to decontamination. However, photochemistry can occasionally produce secondary pollutants that are potentially more dangerous than the parent molecules. Because they exhibit a non-nil quantum yield of direct photolysis, compounds that absorb sunlight and deteriorate as a result can be photo transformed by this method. On the other hand, indirect photochemistry is the conversion of dissolved compounds by a reaction with so-called Photochemically Produced Reactive Intermediates (PPRIs), which does not require the molecules being converted to absorb sunlight.

Hydroxyl ($\cdot\text{OH}$) and carbonate ($\text{CO}_3\cdot$) radicals, excited triplet states of chromophoric dissolved organic matter ($^3\text{CDOM}^*$, where CDOM is the chromophoric portion of the dissolved organic matter, DOM), and singlet oxygen ($^1\text{O}_2$) are the main PPRIs in natural surface waters. PPRIs are created when photosensitisers, or naturally occurring substances including nitrate and nitrite (sources of $\cdot\text{OH}$), as well as CDOM (source of $^3\text{CDOM}^*$, $^1\text{O}_2$, and $\cdot\text{OH}$), absorb sunlight. Additionally, $\text{CO}_3\cdot$ is produced when $\text{HCO}_3^-/\text{CO}_3^{2-}$ are oxidised by $\cdot\text{OH}$ and when CO_3^{2-} are oxidised by $^3\text{CDOM}^*$. In particular, DOM scavenges $\cdot\text{OH}$ and $\text{CO}_3\cdot$, but only to a very minimal extent for $^3\text{CDOM}^*/^1\text{O}_2$. Inorganic carbon, specifically $\text{HCO}_3^-/\text{CO}_3^{2-}$ (for $\cdot\text{OH}$), dissolved oxygen (for $^3\text{CDOM}^*$, to give $^1\text{O}_2$), and collision with the aqueous solvent (for $^1\text{O}_2$) are additional significant scavengers/quenchers. In addition to $\cdot\text{OH}$, $\text{CO}_3\cdot$, $^3\text{CDOM}^*$, and $^1\text{O}_2$, there are other PPRIs that are either less well-known at the moment, for example, longer-lived species like superoxide and organic peroxy radicals, or have the potential to produce harmful secondary contaminants to a greater extent than the PPRIs.

Examples include nitrogen dioxide ($\cdot\text{NO}_2$) and the dibromine (or dibromide) radical ($\text{Br}_2\cdot$), which is mostly formed when bromide in saltwater scavenges $\cdot\text{OH}$ and is a powerful brominating agent, especially for phenols. The latter is primarily produced by the photolysis of nitrate in combination with $\cdot\text{OH}$

and by the oxidation of nitrite by $\cdot\text{OH}$. Other $\cdot\text{NO}_2$ production methods involve the oxidation of nitrite by either $^3\text{CDOM}^*$ or irradiation Fe(III) oxides.

A nitrating/nitrosating agent called NO_2 is used to create hazardous nitroderivatives from aromatic chemicals, as well as poisonous and probably mutagenic/carcinogenic nitrosoderivatives from amines and amino acids. Although NO_2 isn't the only nitrating agent that could be present in an aqueous solution, it is most likely the one that will be active during photonitration reactions under circumneutral conditions. In addition, research on the (photo) nitration pathways of phenols and other aromatic compounds has discovered a wide variety of nitrating agents ($\cdot\text{NO}_2$, HNO_2 , HOONO , H_2OONO^+ , and potentially also N_2O_4), although the majority of them tend to only be active at an acidic pH. Although the precise (photo)nitration pathways and the reactive species involved in (often acidic) atmospheric waters may still be up for debate, in the case of natural surface waters, $\cdot\text{NO}_2$ is more likely to play a significant role.

In natural waters exposed to sunlight, nitrate photolysis and nitrite oxidation by OH result in the production of the nitrating and nitrosating agent i.e. NO_2 . In ordinary natural water conditions, the nitrate process would typically be in charge, with the exception of when $(\text{NO}_2^-) > 0.1 (\text{NO}_3^-)$. Naturally, increased nitrate and nitrite concentration values are particularly favourable for the occurrence of $\cdot\text{NO}_2$. Because minor positive and negative effects cancel each other out, inorganic carbon has little impact on the steady-state ($\cdot\text{NO}_2$), whereas increased DOC has a significant negative impact on the incidence of $\cdot\text{NO}_2$. Organic matter does, in fact, compete with nitrate and nitrite for sunlight irradiance and, thus, for the generation of $\cdot\text{OH}$. Additionally, DOM directly scavenges $\cdot\text{NO}_2$ and the $\cdot\text{OH}$ required for NO_2 oxidation.

Here, it is proposed that bromide found in saltwater and seawater would favour the oxidative processes caused by NO_2 (such as glutathione nitrosation) by reducing the role of OH and increasing the role of NO_2 . In fact, bromide makes NO_2 oxidation by $\text{Br}_2\cdot$ possible, providing an additional source of NO_2 . Under these circumstances, the Br/Br₂ couple functions as an efficient electron shuttle between $\cdot\text{OH}$ and NO_2 .

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